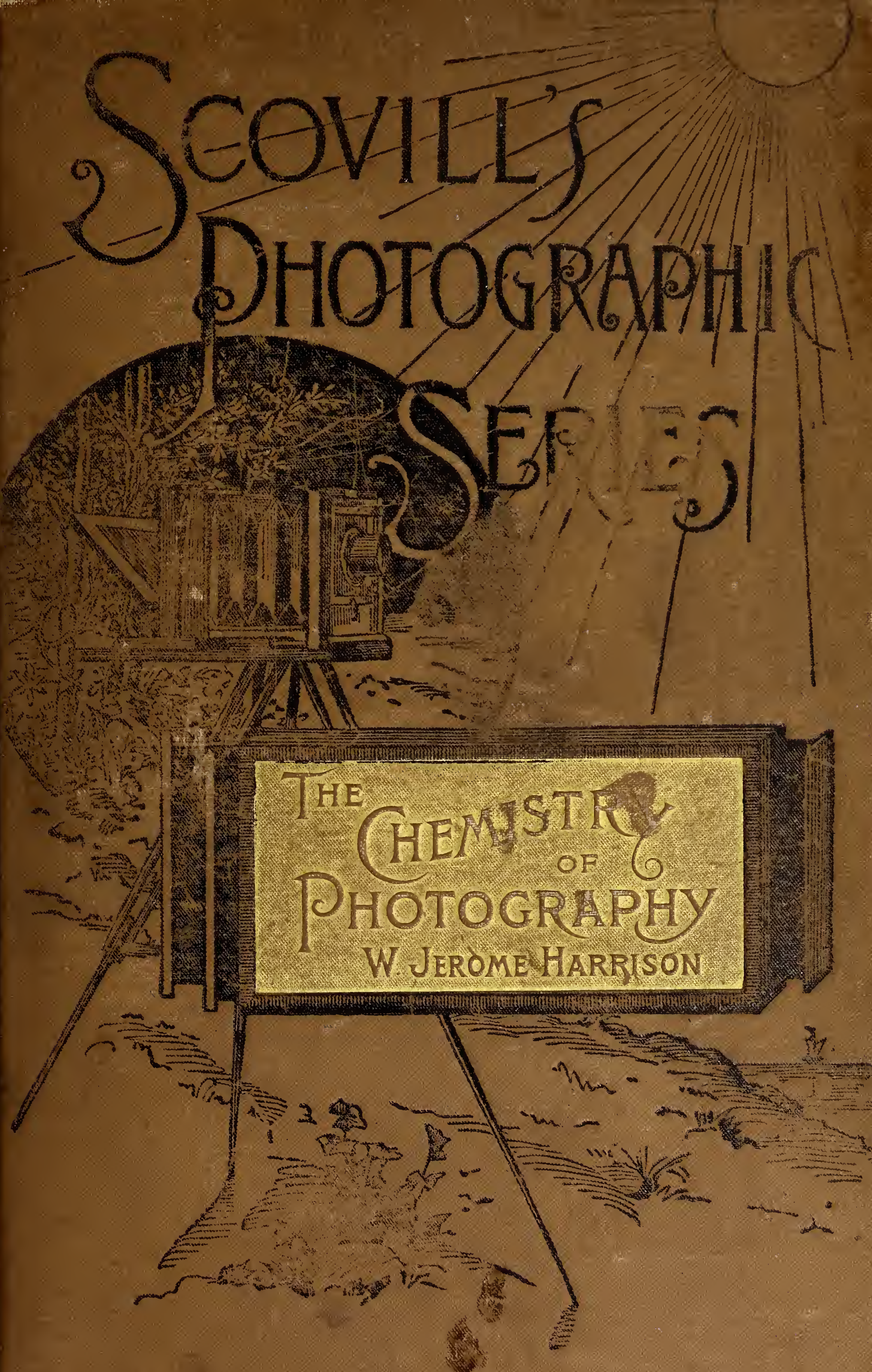

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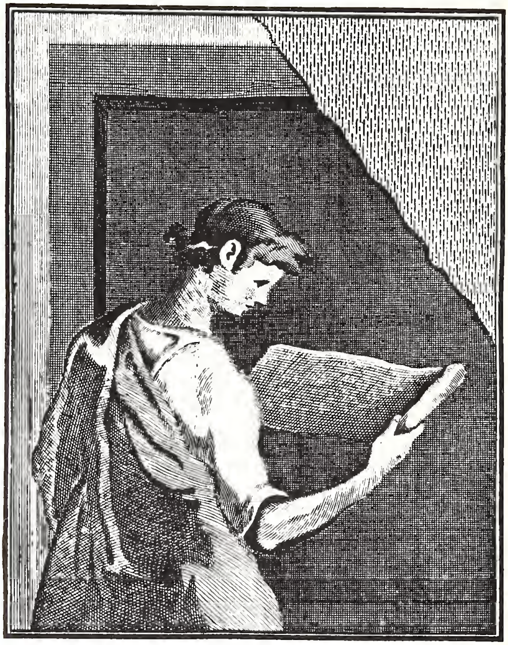

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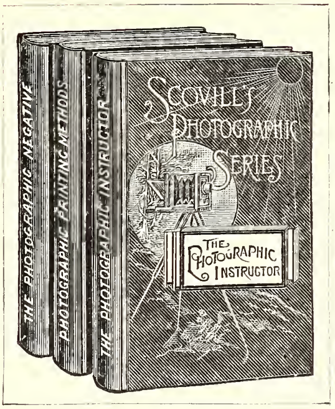
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THE CHEMISTRY

OF

PHOTOGRAPHY

BY

W. JEROME HARRISON, F. G. S.

Chief Science Demonstrator for the Birmingham School Board,
England ; Author of the "History of Photography,"
"Photography for All," "Chemistry for
Beginners," Etc., Etc.

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PREFACE.

The object of this book is to assist in the abolition of "Photography by Rule of Thumb."

The study and practice of the "light science" (as *Cuthbert Bede* playfully styled it forty years ago) ought to be educational as well as recreative. But even from the point of view of the man who cares nothing for photography save as a means of making pictures, it cannot be doubted but that the student who thoroughly understands his tools, and who is able to give "a reason for every rule," will turn out a far higher percentage of technically successful work than one to whom all chemicals are merely "portions of matter"; and to whom every change, every reaction is "magic or mystery."

Familiarity with our modern miracles has, it is true, bred contempt in the minds of many; but every true craftsman tries to get below the surface of things, and to understand the nature of his materials and the way in which they act and interact.

In my account of many of the chemical processes employed in photography, I have treated the subject historically as well as scientifically. For I think that we ought to recall as often as possible the names of the many workers who have helped to place photography on its present high footing as "the handmaid of all the sciences"; and besides, it will generally be found that the pith of a matter is most forcibly presented in the words of the man who was the actual discoverer.

I wish to take this opportunity of expressing the special debt which I owe to photography for the many kind friends with whom it has brought me into relation in both hemispheres; and I wish to thank those friends for their kind appreciation of my labors. If this book—used either as a text-book or as a work of reference—should prove in any way useful to the daily increasing fraternity of the "lovers of light," I shall esteem myself amply repaid for the time and pains (not inconsiderable) which I have expended upon its preparation.

WILLIAM JEROME HARRISON.

Birmingham, England, November, 1892.

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INTRODUCTION.

There can be little doubt but that the photographers of twenty years ago were better chemists than the photographers of to day. Our work is made easy for us by the manufacturers of pure chemicals and excellent dry plates; but the labors of our predecessors were not without their recompense; and although we have gained much in convenience by being no longer under the necessity of preparing our own chemicals, and studying the behavior of the silver bath, yet we have also, to a large extent, lost the love of experiment and research which enabled the last generation of photographers to make such remarkable advances.

No one will deny that a knowledge of chemistry is absolutely necessary to the proper comprehension of photographic processes. Photography is, indeed, but a branch of applied chemistry, so far as most of its manipulations are concerned; and the photographer who is ignorant of this science is only a worker "by rule of thumb." But chemistry itself has advanced very rapidly—has been almost revolutionized, indeed—during the last quarter of a century. It was with pleasure, therefore, that I acceded—a year or two ago—to the request of the editor to contribute to the Photographic Times a series of articles upon modern chemistry, considered more especially in its relations to photography: these articles were followed by others in which photographic materials and processes were treated from a chemical point of view; and the present book consists of these contributions, with such alterations and additions as have been found necessary.

The Chemistry of Photography.

CHAPTER I.

MATTER AND FORCE.

Existence of Matter.—To all substances which are able to affect any of the senses we give the name of *Matter*. Thus matter is a general name for everything which helps to compose the crust of the Earth and its liquid and gaseous envelopes —the ocean and the air. Then there is matter external to our Earth. Our eyes tell us of the existence of countless heavenly bodies—the sun, moon, and stars—and these are connected together by a mysterious kind of matter called the ether, of which we know very little, but which fills all the space between.

General Properties of Matter.—Besides the fact that matter always appeals to the senses, we recognize its existence by the fact that it possesses certain *general* properties, or properties which are common to all kinds of matter.

Thus all matter has *weight*. A cubic foot of air weighs nearly 1¼ ounces; and a cubic foot of the lightest kind of matter known—the gas called hydrogen—weighs nearly thirty-five grains.

Divisibility—or the capability of being divided—is another characteristic of matter. Some solids possess this property in a very marked degree; thus gold can be beaten out so thin that it would take three hundred thousand leaves laid one upon another to make a thickness of one inch. A grain in weight of the odoriferous solid called musk will scent a room for years, with little, if any, perceptible diminution in weight. How extremely small the particles must have been, which, proceeding from the musk, spread through the air and so caused the odor!

But it is when solids are dissolved in liquids, or heated till they change into gases, that the most remarkable facts about the divisibility of matter become known. A very small lump of sugar will give a perceptibly sweet taste to a quart of water. There must be tiny pieces of sugar in each drop of the water, though they are so small as to be invisible. As much strychnine as can be taken up by the point of a needle will give a distinctly bitter taste to the whole of a pint of water; and a single drop of any of the aniline dyes will color a large quantity of the same liquid.

Extension, or *Impenetrability*, expresses that property of matter in virtue of which it takes up space, or occupies room. Two things cannot be in the same place at the same time.

Porosity implies that all substances possess pores or hollow spaces. Solids vary in their porosity, from those like sponge —which is highly porous—to glass, in which the pores are very few and small. The porosity of liquids can be shown by dissolving a small quantity of salt or sugar in a given bulk of water contained in a glass vessel. When the solid has all dissolved, it will be found that the liquid containing it occupies no more space than it did before the solid was added. We can only explain this by supposing that the solid becomes divided into extremely small parts, and that these find room in the pores of the liquid.

The porosity of gases can be proved by putting a few grains of solid iodine into a glass flask and then carefully corking it. When the flask is gently heated the iodine will be converted into a violet vapor which will fill the flask. Thus the flask will now be full of two gases—air, and iodine vapor—and this can only be by the latter finding room in the pores of the former.

Special Properties of Matter.—But while all matter has certain properties—such as weight, extension, etc.—in common, each kind of matter is *distinguished* by possessing certain properties, which the other kinds do not. Thus the *color* of matter varies greatly; and in hardness, solubility, and many other points there is great diversity. It is the province of the chemist to make himself acquainted with these similarities and dissimilarities of matter, for he is thereby enabled to recognize the different kinds of matter, and to distinguish them one from another.

The Three States of Matter.—Matter can exist in three states—the solid, the liquid, and the gaseous. Moreover it is possible by the addition or subtraction of heat, to change the state of almost every substance. Thus, taking water in the liquid state, we can by raising its temperature to 212 deg. F., convert it into water-gas (or steam); while by withdrawing heat until the temperature is reduced to 32 deg. we can cause it to assume the solid state known as ice.

Matter is indestructible. It is impossible to destroy or entirely get rid of any portion of matter whatever. We may break, burn, or dissolve a substance, or change its appearance in many ways, but we cannot destroy it. We can prove this by showing that the *weight* of the original substance is always present. Thus when a candle burns, the matter forming the tallow of which it is composed is not destroyed. Tallow is mainly composed of the two elements hydrogen and carbon. The hydrogen and the carbon each unite with the oxygen of the air to form, respectively, water-vapor and carbonic acid gas. These gaseous products mingle with the air and usually escape unseen, while the candle disappears. But if, by chemical means, we arrest the escaping products, we shall find that their weight will *exceed* that of the candle, for they will include all the matter which formed the candle, and in addition some oxygen gas from the air. Thus we do not destroy the matter composing a candle by the act of burning it, we merely *change* it into other substances—water-vapor and carbonic acid gas.

The Structure of Matter.—The discoveries of modern science have led us to believe that matter consists of exceedingly small parts called molecules. When we take a lump of sugar and grind it in a mortar we obtain numerous *particles* of sugar. Although these particles are small, they are perfectly visible to the eye. But shake up some of these sugar particles in water and they become invisible; the sugar *dissolving*, as we say, in the water. It is in the water, but it is now in pieces so small—called *molecules*—that they cannot be distinguished even by the aid of the most powerful microscope. Thus we regard every portion of matter, whether solid, liquid, or gaseous, as composed of an enormous number of small parts or molecules.

Although we cannot see these molecules, yet mathematicians and physicists have attempted to estimate their size, and Sir William Thomson states that "if a drop of water could be magnified until it appeared the size of the Earth, then the molecules of which it is composed would be visible, and would be of a magnitude somewhere between that of a grain of sand and cricket balls."

It is needless to say that we can never hope to attain such a power of magnification, and therefore we can never hope to see the molecules. Yet, thanks to the researches of the chemist and the physicist, we are as sure of their existence, and can reason upon their powers and properties with as much certainty as if we could handle and see them individually.

Molecular Motion.—No molecule forming part of any portion of any kind of matter is ever at rest. In a solid the motions of the molecules are necessarily much restricted by the force of cohesion, but in a liquid they have more freedom and can roll over one another; while in a gas the course of any molecule is only checked by its concussion with its neighbors, or by the sides of the vessel or room in which the gas happens to be contained.

Molecular motion is usually of a vibratory or to-and-fro motion, like that of the prongs of a tuning-fork. But the vibrations of the molecules do not affect our senses in the same way as the vibrations of the tuning-fork. The impressions which are produced by molecular motion are those of *heat* and *light*.

When a piece of iron feels cold it is because the molecules of the iron are vibrating very slowly as compared with the molecules of which our skin is composed. When the same piece of iron feels hot, it is because the rapidity of motion of its molecules has in some way or other been greatly increased. Lastly, when the iron becomes red, or even white hot, it is due to the fact that the iron molecules are vibrating with almost inconceivable rapidity, and are then able to produce waves of light in the ether which lies between the iron and our eyes. These waves in the ether traveling through the intervening space, at last reach the retinal expansion at the back of the eye, where they excite fresh vibrations in the optic nerve, and these traveling along that nerve to the brain, produce there the sensation of light.

Changes Due to Molecular Motion.—The effect of heat upon a body is to throw its molecules into more rapid vibration. This motion causes each molecule to push away its neighbor, with the result that the body *expands* or becomes larger.

If the heat be increased beyond a certain point, we have learnt that solids are changed into liquids, and liquids into gases. A still further increase of heat may produce a still more remarkable change. By heating many substances it is possible to convert them into two or more new substances of very different appearance and properties. Thus, if a little of the "red precipitate" of the drysalters' shops be strongly heated in a glass tube, it entirely disappears and we have in its place two substances known as "oxygen" and "mercury." The explanation of such changes belongs to the science of chemistry.

The Forces of Nature.—Although we cannot conceive of "force" apart from "matter," nor of the existence of matter unacted on by force, yet we believe them to be radically different. Force is without weight—a body when hot weighs no more than when cold—and is unable to affect the senses except through the medium of matter.

The forces of nature have been classified as follows:

I.—THE PHYSICAL FORCES.

Gravity,
Electricity,
Magnetism,
Heat,
Sound,
Light,
Cohesion.

These physical forces are able to *act at a distance.* To the action of gravity and of light, for instance, no limits can be set; the effects of these forces extend far beyond even our solar system.

Sound can travel by means of vibrations of the air, but not by the ether, and earthly sounds are, therefore, confined within the limits of our atmosphere.

Cohesion is unlike the other physical forces in being unable to act save at comparatively small distances, but even these distances are wide, as compared with those over which the chemical force is able to exert its influence.

The physical forces do not commonly change the properties or composition of the matter upon which they act. For example, a piece of iron may be allowed under the influence of *gravity* to fall from any height; it may be melted by *heat;* after cooling it can be *magnetised* by causing a current of *electricity* to flow round it; yet, after all these physical forces have acted upon it, the iron is still unchanged in its nature and properties.

II. The Chemical Force.—The chemical force stands apart from all the other forces in two respects. It is quite unable to act at even extremely small distances; indeed it seems necessary to bring the molecules of one body into actual *contact* with those of another before chemical action can take place between them. For this reason it is hardly ever possible to get two *solids* to unite chemically; one or, better, both must be brought into the liquid or the gaseous state.

Then the chemical force always produces a change in the composition, and usually in the properties of the matter upon which it acts. When sulphuric acid, for example, is poured upon sugar, violent chemical action takes place, gases are given off, and a black porous solid remains.

CHAPTER II.

THE CHEMICAL ELEMENTS.

Definition of Chemistry.—Chemistry is the science which studies the composition of matter, and which endeavors to explain the processes by which changes are effected in its composition.

So great a mass of chemical knowledge has now been accumulated that a lifetime might be spent in the study of a single section of chemistry. In these articles we shall only consider those principles and facts of chemistry which bear more especially upon photography.

THE TWO GREAT DIVISIONS OF CHEMISTRY.

The science of chemistry is divided into two main parts; viz:—

I. INORGANIC CHEMISTRY, dealing with substances belonging to the Mineral Kingdom, *i. e.*, with matter having no parts or organs; and,—

II. ORGANIC CHEMISTRY, which treats of compounds many of which exist ready formed in animals or plants—organized beings.

Organic Chemistry is also known as the chemistry of the Carbon Compounds, because Carbon forms a part of every substance of which this division of chemistry treats.

Nature of the Chemical Elements.—We are acquainted with about seventy substances, each of which we believe, in the present state of our knowledge, to be composed of one kind of matter only, and that different from all other kinds. These seventy substances are known as the chemical elements. Thus an element may be defined as a *simple substance*, composed of one kind of matter only.

Gold is a good example of an element. Out of pure gold no one has succeeded in getting anything but gold.

It is impossible to change any one element into any other element. This was the mistake made by the *alchemists*, who in the Middle Ages tried so hard to transmute the baser metals, such as lead, into the precious metals gold and silver. The molecules of lead are totally different in their properties from the molecules of gold, and it is equally impossible to change lead into gold, or gold into lead.

Still there is no reason why the number of the elements should not any day be increased or diminished. Within the last ten years six new elements have been found, though all these are of rare occurrence. On the other hand, it is just possible that the continued researches of chemists may end in proving that some of the substances we now consider elementary, are really compounds of two or more other elements. It has even been suggested that there is only *one* true element, of which all the others are composed in varying proportions and under varying conditions ; but we are still very far from being able to prove this.

TABLE OF THE CHEMICAL ELEMENTS.

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
*Aluminium	Al.	27	*Gold	Au.	196
Antimony	Sb.	120	*HYDROGEN	H.	1
ARSENIC	As.	75	Indium	In.	113.4
*Barium	Ba.	137	*IODINE	I.	127
Beryllium	Be.	9	*Iridium	Ir.	192.5
Bismuth	Bi.	208.2	*Iron	Fe.	56
BORON	B.	11	Lanthanum	La.	138.5
*BROMINE	Br.	80	*Lead	Pb.	206.5
*Cadmium	Cd.	112	Lithium	Li.	7
Cæsium	Cs.	133	*Magnesium	Mg.	24.4
*Calcium	Ca.	40	Manganese	Mn.	55
*CARBON	C.	12	*Mercury	Hg.	200
Cerium	Ce.	140.5	Molybdenum	Mo.	95.5
*CHLORINE	Cl.	35.5	Nickel	Ni.	58.6
*Chromium	Cr.	52	Niobium	Nb.	94
Cobalt	Co.	58.6	NITROGEN	N.	14
*Copper	Cu.	63.2	Norwegium	Ng.	214
Decipium	Dp.	159	Osmium	Os.	198.6
Didymium	Di.	146	*OXYGEN	O.	16
Erbium	Er.	165.9	*Palladium	Pd.	105.7
*FLUORINE	F.	19	*PHOSPHORUS	P.	31
Gallium	Ga.	68.8	*Platinum	Pt.	194.4

TABLE OF THE CHEMICAL ELEMENTS—*Continued.*

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
*Potassium	K.	39	TELLURIUM	Te.	125
Rhodium	Rh.	104	Terbium	Tb.	148.8
Rubidium	Rb.	85.3	Thallium	Tl.	204
Ruthenium	Ru.	104	Thorium	Th.	233.4
Samarium	Sm.	150	*Tin	Sn.	118
Scandium	Sc.	44	Titanium	Ti.	48
*SELENIUM	Se.	79	Tungsten	W.	184
*SILICON	Si.	28.2	*Uranium	U.	238.5
*Silver	Ag.	107.7	Vanadium	V.	51.3
*Sodium	Na.	23	Ytterbium	Yb.	172.8
Strontium	Sr.	87.5	Yttrium	Y.	89.8
*SULPHUR	S.	32	*Zinc	Zn.	65.3
Tantalum	Ta.	182	Zirconium	Zr.	90

Symbols.—It is very convenient to use the first letter or letters of the name of an element to represent that element, instead of having to write the entire name. To such letters the name of symbols is applied. Many of the symbols, however, are not derived from the ordinary names of the elements, but from their Latin names.

Thus we have:

Ordinary Name.	Latin Name.	Symbol.
Antimony	Stibium	Sb.
Copper	Cuprum	Cu.
Gold	Aurum	Au
Iron	Ferrum	Fe
Lead	Plumbum	Pb.
Mercury	Hydrargyrum	Hg.
Potassium	Kalium	K.
Silver	Argentum	Ag.
Sodium	Natrium	Na.
Tin	Stannum	Sn.

Each symbol stands for a single atom of the element which it represents. When it is desired to indicate more than one atom, this is done by placing a small figure below and to the right of the symbol. Thus O, O_2, O_4, represent one, two and four atoms of oxygen respectively.

Atomic Weights.—The figures placed opposite to the symbols of the elements in the table above, represent the *relative weights* of the atoms of the various elements. Thus we believe that an atom of oxygen is sixteen times, and an atom of mercury two hundred times as heavy as an atom of hydrogen. Thus each symbol represents something more than the mere name of the element for which it stands. It also indicates a certain proportion by weight of that element; indicating, in fact, its atomic weight as well as its name.

Classification of the Elements.—The main division of the elements is into metals and non-metals. In the above table the names of the fifteen non-metals are printed in capital letters. There are three characters by which metals are commonly distinguished, viz.: (1) the possession of metallic luster, (2) they are good conductors of heat, (3) and good conductors of electricity; these three properties are never found united in a non-metal.

At the ordinary temperature of the air five of the elements are gaseous—oxygen, hydrogen, nitrogen, fluorine and chlorine; two are liquids—bromine and mercury; and the remaining sixty-three are solids. Every element has been liquefied by heat with the single exception of carbon.

By means of great cold combined with great pressure, all the gaseous elements can be reduced to the liquid and even to the solid state.

Thirty of the elements are designated rare, being found only in very small quantities. Oxygen is by far the most abundant element, constituting one-fifth of the air, eight-ninths (by weight) of water, and one-half of the solid crust of the Earth.

In the substances more or less commonly employed in photography about one-half of the chemical elements are present. They are distinguished in the table by an asterisk (*).

Chlorous and Basylous Elements.—The elements differ widely among themselves in their electrical properties. The metals are good conductors of electricity, allowing it to pass more or less freely; while the non-metals such as sulphur, silicon, etc., are non-conductors. It has been thought possible that it is the force of electricity which determines the chemical combination of the elements. Thus in the case of water we know that the hydrogen atoms are electro-positive as compared with the oxygen atoms which are electro-negative—for it is *unlike* kinds of electricity (positive and negative) which attract one another. There are eight of the elements—Chlorine, Bromine, Iodine, Fluorine, Oxygen, Sulphur, Selenium, and Tellurium—which are electro-negative when compared with any of the remaining sixty-two elements. These eight elements are called chlorous or negative because chlorine is their type. The other sixty-two elements are called *basylous* (or positive).

The chemical union between any two or more chlorous elements is usually *weak*, and such compounds are easily decomposed. On the contrary, the union of a chlorous with a basylous element forms a compound which is more or less stable.

CHAPTER III.

TERMS EMPLOYED IN CHEMISTRY.

Chemical Formulæ.—We have learned that the names of elements are represented by letters called symbols. The "symbols" of compound substances are formed by placing in juxtaposition the symbols of the elements of which the compound is composed. To such a collection or *group* of symbols the term *chemical formula* is applied.

Thus chloride of silver, which is composed of one atom each of the elements silver and chlorine, is represented by the formula AgCl. Every molecule of sulphuric acid contains seven atoms—two of hydrogen, one of sulphur, and four of oxygen—accordingly its formula is H_2SO_4. If we desire to represent more than one molecule, this may be done by placing a large numeral in front of the formula. Thus 6 AgCl will stand for six molecules of silver chloride; 4 H_2SO_4, for four molecules of sulphuric acid.

Molecular Weights.—The weight of any molecule is found by adding together the weights of the atoms of the respective elements of which it is composed. Thus, supposing it is required to find the molecular weight of silver nitrate, $AgNO_3$.

Element.	Atomic Weight.		No. of Atoms.		
Ag.	108.	x	1	=	108.
N	14	x	1	=	14
O_3	16	x	3	=	48
		Molecular Weight,		=	270

Chemical Nomenclature.—The large number of *names* used in chemistry has led to the introduction of systems of framing these names which are very useful, because we then get as much information out of each name as possible. Still it must not be forgotten that there are exceptions to every rule, and many names have been applied to chemical substances which later discoveries have shown to be incorrect.

All metals discovered in modern times have been given names ending in—*um*, as magnesium, chromium, etc. But here at once we meet with exceptions, for the elements selenium and tellurium—thought to be of a metallic nature at the time of their discovery—have since been found to be more properly classed with the non-metals.

Binary Compounds.—A compound containing two elements only is called a binary compound. All the chemical names of such compounds end in—*ide.* Thus "red precipitate"—which is composed of oxygen and mercury—is known as mercuric oxide; the name of the metal being formed into an adjective and placed first, while the non-metal has the affix —*ide*—added to the first syllable of its name. Thus the name—mercuric oxide—tell us that the red precipitate is composed of mercury and of oxygen, and of these two elements only. But the same two elements frequently combine with one another in varying proportions, so forming two distinct binary compounds which it is necessary to distinguish from each other. In such a case the adjectival termination—*ic*—is assigned to the compound which contains the larger proportion of the non-metal; while to that which has *less* of the non-metal the termination—*ous*—is appended. Thus we have one atom of tin and two atoms of chlorine forming *stannous* chloride; while one atom of tin and four atoms of chlorine form *stannic* chloride.

It may even happen that the same two elements form more than two compounds. To that compound which has least of the non-metal we then give the prefix "hypo-"; to that which has most the prefix per-. Sometimes "sub-" is used instead of "hypo."

Thus we have—

Nitrous Oxide—containing two atoms of nitrogen and one atom of oyxgen (N_2O).

Nitric Oxide—containing two atoms of nitrogen and two atoms of oxygen (N_2O_2).

And,—

Nitric Per-oxide—containing two atoms of nitrogen and four atoms of oxygen (N_2O_4).

And again,—

Hypo-chlorous oxide—containing one atom of oxygen and two atoms of chlorine (Cl_2O).

And,—

Chloric Per-oxide—containing four atoms of oxygen and two atoms of chlorine (Cl_2O_4).

Anhydrides.—There are certain oxides which when added to water, form *acids;* these oxides are termed "anhydrides." Thus we have carbonic anhydride, composed of one atom of carbon and two atoms of oxygen; and nitric anhydride, composed of two atoms of nitrogen and five atoms of oxygen, etc.

Acids.—The term acid was at first applied to all substances having a sour taste like vinegar (which is dilute acetic acid). As used by chemists the term is now given to "any compound containing one or more atoms of hydrogen, which are displaced when a metal is presented to the compound in the form of a hydrate." Thus, if we mix hydrogen chloride ($H\ Cl$) with potassium hydrate ($K\ H\ O$), the metal potassium displaces the hydrogen and forms potassium chloride (KCl), while the displaced hydrogen unites with the oxygen to form water (H_2O). Hydrogen chloride is, therefore, called an *acid.* It is still true, however, that the majority of acids are sour-tasting substances. Another simple test for acids is the power which they possess of turning blue litmus red. Litmus is a vegetable coloring matter (obtained from a kind of lichen) which is used either in solution or on test-papers which have been dipped into litmus solution and then dried.

Bases.—The term base is applied to certain compounds which, when they combine with acids, form SALTS. The best-known bases are (1) certain metallic oxides, such as potassium oxide (K_2O), zinc oxide ($Zn\ O$), etc.; (2) certain metallic hydrates, such as sodium hydrate ($Na\ H\ O$); (3) certain other compounds, of which only ammonia ($N\ H_3$) need here be named. The *hydrates*, or hydroxides, result from the combination of metallic oxides with water. Thus:—

Barium oxide *combines with* water *to form* barium hydrate.

Salts.—The chemical compound which results from the mutual action of an acid and a base, is called a *salt; e.g.*,

Ammonia	*combines with*	hydrochloric acid	*to form*	ammonium chloride.
(*base*)		(*acid*)		(*salt*)

Water of Crystallization.—The presence of water is necessary to the crystallization of many salts. When the water is driven off by heat, the crystal falls to powder. Each such salt unites with a certain definite quantity of water to form its crystals, and the union is an example of molecular combination. In the absence of the water the salt is said to be in the *anhydrous* state. Thus silver sulphate (Ag_2 SO_4) is naturally an anhydrous salt, not requiring the aid of water to form its crystals; but the green crystals of ferrous sulphate consist of Fe SO_4 combined with seven molecules of water. Its formula may be written Fe $So_4 + 7H_2O$; or Fe SO_4, $7H_2O$. At a temperature of 300 deg. C. all the water is driven off, and a white powder remains which consists of Fe SO_4 only. As chemists almost invariably sell such salts in their crystallized state, it is necessary—in calculating the amount of each constituent in a given weight of the salt—to take into account the water of crystallization.

CHAPTER IV.

CHEMICAL LAWS AND THEORIES.

Chemical Combination.—The introduction of the delicate form of weighing machine known as the *balance* into the study of chemical changes inaugurated a revolution in the science of chemistry. Among other things it proved that matter is indestructible—that when one form of matter disappears, an equal weight of some other form is produced. But it also showed that when the different elements, or compounds, enter into chemical combination with one another. they do so in fixed and unalterable proportions by weight and by volume.

Law of Constant Proportions.—Suppose we purchase a hundred specimens of pure nitrate of silver, each sample weighing 270 grains, prepared by as many chemists, living perhaps in different countries. Then analysis proves that every one of these hundred specimens is composed of 108 grains of metallic silver, 14 grains of nitrogen, and 48 grains of oxygen. It is the same with every other chemical compound, the proportions of each element of which it is formed are *constant.*

Law of Multiple Proportions.—Although, in the same substance, the elements which compose it bear a fixed proportion, by weight, to each other, yet it is frequently the case that the same elements can combine with each other in *different* proportions. But in each case the compound produced is distinct in its nature and properties. The binary compounds resulting from the chemical union of nitrogen with oxygen are an excellent example of this. No fewer than five such compounds are known which are shown in the following table :

NAME.	Formula.	Containing parts of Nitrogen.	Containing parts of Oxygen.
Nitrous Oxide........	N_2O	28	16
Nitric Oxide..........	N_2O_2	28	32
Nitrous Anhydride....	N_2O_3	28	48
Nitric Peroxide.......	N_2O_4	28	64
Nitric Anhydride.....	N_2O_5	28	80

Each of these five compounds is composed of the same two elements, and yet they are five substances differing greatly in their properties. In the table it will be noticed that the varying proportions of the oxygen are all multiples of the atomic weight of oxygen—16, and in all such cases the proportions are found to be simple multiples of some common factor.

Atomic Theory.—It was such considerations as these, which, in the early part of the present century, led Dalton to the discovery of the atomic theory. This theory considers matter to be composed of extremely small parts called *atoms*, which cannot by any means be divided: as, in fact, the word atom—that which cannot be cut—implies.

The atoms do not all possess the same weights—those of one element are, as a rule, either heavier or lighter than those of another element; thus an oxygen atom is sixteen times, and a nitrogen atom fourteen times as heavy as an atom of hydrogen. We know this to be the case because a pint, say, of oxygen weighs sixteen times and a pint of nitrogen fourteen times as much as a pint of hydrogen. Now, we have every reason to believe that, under similar conditions, there are exactly the same number of atoms contained in equal volumes of these gases. Therefore each individual atom of O must be 16, and of N 14 times as heavy as each atom of H.

Chemical combination consists in the union of atom with atom, to form *molecules*, which are the smallest portions of matter capable of independent existence. Since an atom is "the smallest quantity of an element, by weight, which can enter into, or be expelled from a chemical compound," we see why chemical combination, or decomposition, always takes place in accordance with some multiple of the atomic weights. It is not possible, for example, for 24 parts by weight of oxygen to unite with 28 parts of nitrogen, for (dividing each by their atomic weights) that would necessitate $1\frac{1}{2}$ atoms of the former uniting with 2 atoms of the latter, and fractions of an atom cannot exist.

Mixtures.—When two or more elements are simply mixed together, without the exercise of chemical force or affinity, each element retains its own properties, and can be recognized by these as a part of the mixture. Thus, let iron filings be rubbed up in a mortar with some sulphur. A yellowish powder is obtained in which the particles of iron and of sulphur can still be plainly distinguished by the aid of a magnifying glass; and by passing a magnet through the mixture the iron can be readily separated from the sulphur.

Chemical Compounds.—In the formation of a true compound the chemical force is engaged, and the result of its action is the formation of a new substance, whose properties are usually very different from those of the elements which united to form it. Thus let the *mixture* of iron and sulphur referred to above be strongly heated. The heat will stimulate the chemical affinity or liking of the iron for the sulphur, and the two elements will unite to form a *compound* which is known as sulphide of iron. This sulphide of iron is a blackish solid in which neither iron nor sulphur can be detected by the microscope, and it is quite unaffected by a magnet.

Common and Scientific Names.—Many chemical compounds are known by more than one name. It has frequently happened that a substance has been long in use before the discovery of its true chemical composition, and, consequently, before a correct name, according to the ideas of chemists, could be given to it. The old name, given to the substance before its true nature was known, often survives and is used for commercial purposes.

In the following table the old and often commercial names of the various substances are given in alphabetical order, and opposite each is placed the name by which it is now more correctly known in modern chemistry:

Old or Commercial Name.	Modern or Scientific Name.	Formula.
Alum.	Aluminum Potassium Sulphate.	$Al_2(SO_4)_3$, K_2SO_4, $24H_2O$.
Aquafortis	Nitric Acid.	HNO_3.
Bichromate of Potash.	Potassium Bichromate.	$K_2Cr_2O_7$.
Blue Vitriol.	Copper Sulphate.	$Cu\ SO_4$.
Chalk (precipitated).	Calcium Carbonate.	$Ca\ CO_3$.
Common Salt or Rock Salt.	Sodium Chloride.	$Na\ Cl$.
Copperas.	Ferrous Sulphate.	$Fe\ SO_4$.
Green Vitriol.		
Proto-sulphate of Iron.		

Old or Commercial Name.	Modern or Scientific Name.	Formula.
Corrosive Sublimate, or Bichloride of Mercury.	Mercuric Chloride.	$Hg\ Cl_2$.
Hartshorn, or Spirits of Hartshorn.	Ammonia.	$N\ H_3$.
Hyposulphite of Soda.	Sodium Thiosulphate.	$Na_2\ S_2\ O_3$.
Lunar Caustic.	Silver Nitrate.	$Ag\ N\ O_3$.
Muriatic Acid, or Spirits of Salt.	Hydrochloric Acid.	$H\ Cl$.
Muriate of Ammonia.	Ammonium Chloride.	$N\ H_4Cl$.
Oil of Vitriol.	Sulphuric Acid.	$H_2\ SO_4$.
Permanganate of Potash.	Potassium Permanganate	$K\ Mn\ O_4$.
Pyrogallic Acid.	Pyrogallol.	$C_6H_6O_3$.
Perchloride of Iron.	Ferric Chloride.	$Fe_2\ Cl_6$.
Red Prussiate of Potash.	Potassium Ferricyanide	$K_3\ Fe(CN)_6$.
Sal-ammoniac	Ammonium Chloride.	$N\ H_4\ Cl$,
Soluble Gun Cotton.	Pyroxline, or Nitro-cellulose.	$C_6H_8(NO_2)_2O_5$.
Spirits of Wine.	Ethylic Alcohol.	$C_2\ H_6\ O$.
Sulphuric Ether.	Ether.	$C_4\ H_{10}\ O$.
Sulphuretted Hydrogen.	Hydrosulphuric Acid.	$H_2\ S$.
Tannin.	Tannic Acid.	$C_{27}\ H_{22}\ O_{17}$.
Wood Spirit.	Methylic Alcohol.	$C\ H_4\ O$.
Yellow Prussiate of Potash.	Potassium Ferrocyanide.	$K_4\ Fe\ (CN)_6$.
Aqua Regia.	Nitro-hydrochloric Acid.	$HCl + HNO_3$.
Sel D'Or, or Hypo-sulphite of Gold.	Thiosulphate of Gold.	$Au_2\ S_2\ O_3$.
Chrome Alum.	Chromium Potassium Sulphate.	$Cr_2\ (SO_4)_3,\ K_2\ SO_4 + 24\ OH_2$.
Green Vitriol.	Ferrous Sulphate.	$Fe\ SO_4 7H_2O$.
Blue Vitriol,	Cupric Sulphate.	$Cu\ SO_4 5H_2O$.
Prussic Acid.	Hydrocyanic Acid.	$H\ C\ N$.
Caustic Soda.	Sodic Hydrate.	$Na\ HO$.
Caustic Potash.	Potassic Hydrate.	$K\ H\ O$.
Calomel.	Mercurous Chloride.	$Hg_2\ Cl_2$.
Red Precipitate.	Mercuric Oxide.	$Hg\ O$.
Condy's Fluid.	Permanganate of Potash.	$K\ Mn\ O_4$.
Borax.	Sodic Borate.	$Na_2B_4O_7 10H_2O$.

CHAPTER V.

CHEMICAL MANIPULATIONS.

Under this heading come the various operations used in chemistry, such as solution, distillation, etc., operations which the photographer will have to perform very frequently if he aspires to be something more than a drawing-room dabbler. We have no sympathy with the man who buys his developer ready-made, or perhaps uncaps the lens only, and then sends the plate to a professional photographer to be developed.

Solution.—By solution we mean the process which takes place when a solid is converted into the liquid state by the aid of water or some dissolving agent. Thus when we put a piece of solid lump sugar into water we find that in a short time the sugar disappears. The sugar is no longer in the solid state, but becomes itself a liquid, occupying the pores or interspaces between the molecules of the water. That there is some force or mutual attraction acting between the solid and the dissolving liquid seems to be pretty certain, for whereas hyposulphite of soda, for example, is very soluble in water, it will not dissolve at all in alcohol. It is found that certain liquids have a peculiar attraction for a particular class of bodies; thus water is an almost universal solvent for the class of bodies known as *salts*, but will not readily dissolve such bodies as gums, resins and other colloidal substances, whereas ether, alcohol, chloroform, turpentine and other liquids belonging to the organic class of bodies are particularly good solvents for these colloidal bodies, but are bad ones for salts, etc. The best way to dissolve a solid is to powder it in a mortar (Fig. 1) before bringing it into contact with the liquid; this exposes a larger surface to the action of the liquid. The process of solution is also aided by heating the liquid. A given quantity of any liquid cannot at a given temperature dissolve more than a certain quantity of any solid.

When it has dissolved as much as is possible, the liquid is said to be *saturated*. If more of the solid is then added it will remain in the solid state, usually lying at the bottom of the vessel in which the liquid is contained. Although a hot liquid will usually dissolve a solid more rapidly than a cold liquid, yet care must be used in its employment. Thus boiling water will partly decompose ferrous-sulphate, hyposulphite of soda, etc., and generally it may be said that though it is allowable to use the liquid warm it is safer in dissolving the ordinary chemicals employed in photography not to have it boiling. A good plan to dissolve a solid rapidly is to place it in a muslin bag, which is then suspended by a string so as to hang near the top of the bottle containing the liquid in which the solid is to be dissolved. Or a piece of paper may be cut out to fit in the neck of the bottle, and some pin-holes made in the centre; it is then folded up, inserted in the neck of the bottle so that the lower end dips in the liquid, and the powdered solid is placed within it. These plans are advantageous because the saturated liquid is heavy and sinks to the bottom.

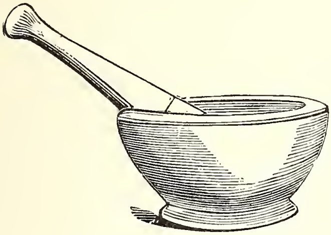


FIG. 1.

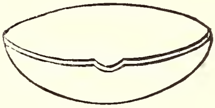


FIG. 2.

Evaporation.—When a substance is in solution we use the process known as *evaporation* to obtain the substance in the solid state. By boiling, or evaporating, the liquid is driven off, leaving the solid substance behind. In evaporating solutions, vessels known as porcelain evaporating dishes (Fig. 2) are used, which are warmed uniformly by being placed on a sand-bath (a round iron or tin dish containing sand), heated by a Bunsen burner; the liquid should be occasionally stirred with a glass rod during evaporation. The Bunsen burner (Fig 3) burns air and gas mixed, giving a hot, smokeless flame; it should be provided with a rose-top to spread out the flame when required.

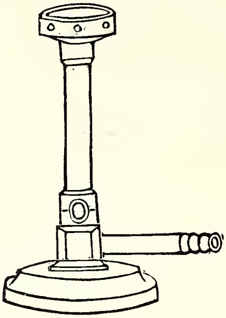


Fig. 3.

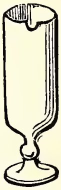


Fig. 4.

Precipitation.—When we mix two clear liquids together we often get a turbidity, caused by the formation of some insoluble matter; the solid formed is known as a precipitate, and the process as precipitation.

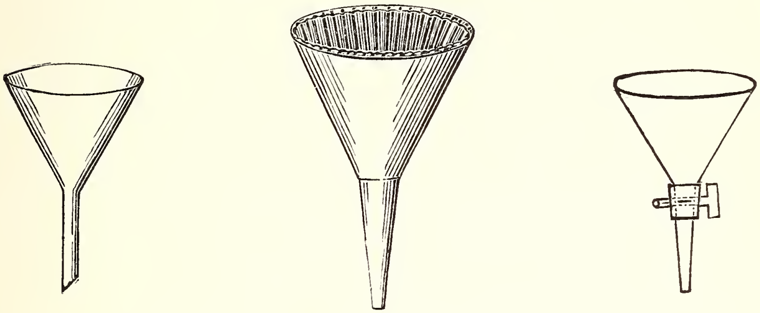
For example, when we mix a solution of silver nitrate and hydrochloric acid together, we get a white, curdy precipitate; this is silver chloride, formed by the chemical reaction between the two substances; it is insoluble in either water or hydrochloric acid, and so it makes its appearance in the solid state.

$AgNO_3$	+	HCl	=	$AgCl$	+	HNO_3
Silver Nitrate.	*joins with*	Hydrochloric Acid	*to form*	Silver Chloride (insol.)	*and*	Nitric Acid

For studying precipitation, test-glasses on feet (Fig 4) are very convenient; or the thin glass tubes called test-tubes may be employed.

Filtration.—When we wish to separate the precipitate from the liquid with which it is mixed, we use the process known as filtration. For this purpose we pour the whole upon some porous body which lets the liquid run through but will not permit the solid matter to pass; the liquid which runs through is known as the filtrate. Porous paper, known as filter paper, is used for this purpose. Only matter *suspended* in water can be removed by filtration; dissolved matter cannot be filtered off.

Filter paper is usually sold in circular pieces; fold the paper in half, then fold again; it is now a quarter-circle; now open it so as to form a hollow paper cone; this cone is fitted into a glass funnel (Figs. 5, 6, 7) and gently moistened with water before passing the liquid through which it is desired to filter. A filter-stand (Fig. 8) is useful to hold the funnel, and the filtrate may be received in a test-glass or in a beaker (Fig. 9).



FIGS. 5, 6, 7.

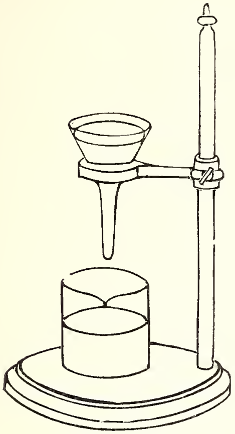


FIG. 8.

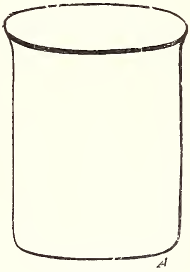
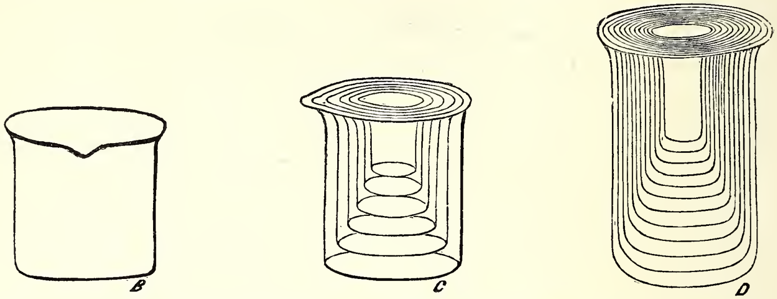


FIG. 9.

Decantation.—For heavy precipitates, and for precipitates which fall to the bottom rapidly, the process of decantation may be employed. The beaker containing the precipitate is allowed to stand for some time until all the solid matter has settled to the bottom. The clear liquid is then carefully poured off, and distilled water added to the precipitate ; the whole is shaken up, and the precipitate is again allowed to settle, and the clear water poured off. This washing is repeated several times, until the precipitate is completely freed from the adhering solution ; this is known as washing by decantation.



Stout glass beakers, *A* and *B*; thin beakers for holding hot liquids, *C* and *D*. The latter are arranged in sets, or nests, fitting one within the other.

Glass vessels shaped like Fig. 10 are very convenient for this sort of work.

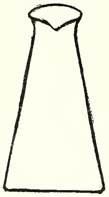


Fig 10.

Distillation.—The process called distillation is used to purify liquids ; or to separate liquids from solids, or from other liquids which boil at different temperatures.

Distillation is effected by boiling the liquid in a retort, cooling or condensing the vapor given off by means of a condenser, and collecting the condensed liquid in a vessel known as a receiver ; the impurities and solid matter remain behind in the retort. Ordinary water contains several impurities in the shape of dissolved solid matter, and this renders it unfit for many chemical purposes ; it therefore has to be distilled to render it pure.

Water may be distilled on a small scale by placing the liquid in a glass flask (Fig. 11), the neck of which is connected with a long glass tube which is surrounded by an outer jacket of glass or tin through which cold water must be continually kept flowing. This piece of apparatus is known as Liebig's condenser. The end of the glass tube is placed within a flask known as a receiver, because it receives the condensed liquid. The water in the retort is heated by a Bunsen burner; the steam given off passes down through the condenser; it is there cooled and condensed, and the distilled water is collected in the receiver. Where large quantities are required, the still is best made of copper, and the spiral tube, or "worm," of tin (Fig. 12).

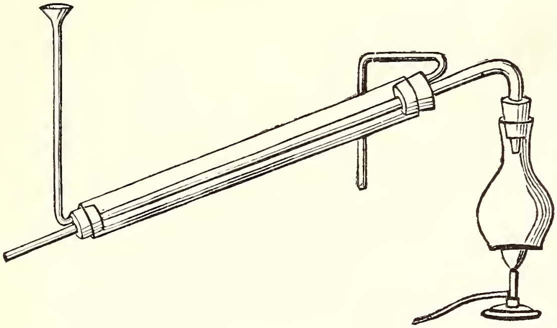


Fig. 11

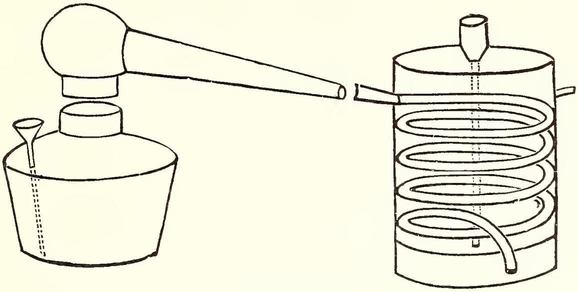


Fig. 12.

Fractional Distillation.—The process of distillation may be made use of to separate or fractionate liquids, which have different boiling points. Suppose we have a mixture of two liquids whose boiling points differ rather widely, say, water and alcohol. Water we know boils at 212 deg. F., whereas alcohol boils at 173 deg. F.; we place the mixture in a retort and heat gently. A vapor is given off and condenses in the receiver, and if we have a thermometer connected with the inside of the retort, we shall see that it stands at about 173 F. This shows us that the alcohol only is boiling, and that our "distillate" is chiefly alcohol; after a time, the thermometer will slowly rise, and steam, or water-vapor, will be given off. Change the receiver and collect the condensed water. By this means we have more or less completely separated the alcohol from the water, and by repeating the process on each of the distillates we can get nearly pure samples of water and of alcohol.

MANIPULATION OF GLASS, GLASS-BLOWING, ETC.

The photographer has often to fit up and make certain pieces of apparatus which require a slight knowledge of the manipulation of glass, and if he has not had previous experience he will usually waste a lot of time and glass before he gains his desired ends. We therefore propose to give a few hints which should enable any one with a little practice to become fairly proficient in the art of manipulating glass.

Kind of Glass to be Employed.—There are two sorts of glass tubing—hard glass and soft glass tube, the latter is the kind most generally used. There are also two varieties of soft glass tubing, one known as lead glass and the other as soda glass. The lead glass tubing is easy to work, but has the unpleasant property of blackening in the reducing flame, so that soda glass is, on the whole, the best sort to use (Fig 13).

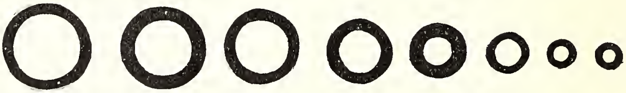


FIG. 13.

Blow-Pipe.—For some things an ordinary Bunsen burner will be sufficient; but it will be found that for many purposes a blow-pipe of some kind will be indispensable. The common mouth blow-pipe known as Black's is very useful, but requires a little practice (Fig 14). It is used in conjunction with a Bunsen burner; the white or gas flame of the Bunsen is employed, and the nozzle of the blow-pipe is placed just inside the bottom part of the flame, and a gentle blast will give you a flame possessing great heating power. The blow-pipe flame consists of two parts, an inner and an outer cone; a point a little beyond the end of the inner cone will be found to be the hottest part of the entire flame. For blow-pipe purposes a continuous blast is necessary. This is obtained by inflating the cheeks and breathing through the nose, filling the cheeks when required from the lungs. Fletcher's "Herepath" blow-pipe with foot blower (Figs. 15 and 16) is a most useful piece of apparatus; but for ordinary purposes it may be dispensed with.

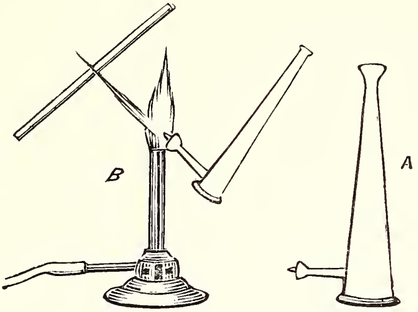


FIG. 14

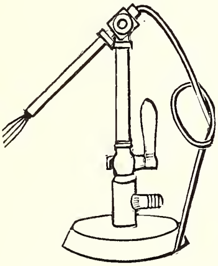


FIG. 15.

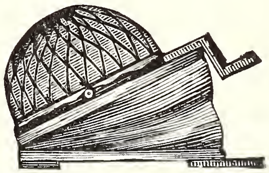


FIG. 16.

To Cut Glass Tubing.—Glass tubing is usually cut by means of a three-cornered or triangular file; a small file with fine serrated edges will be found best. For thin tubes all that is necessary is to draw the edge of the file across the part you wish to cut; then take hold of the tubing on both sides of the cut with the hands (the file mark being uppermost) and, pulling with a slight downward tendency (Fig. 17), the tube will be found to break clean at the file cut. For very thick and strong tubing it will be found necessary to file all around the desired part; then apply a piece of red-hot glass or a hot poker to the cut and it will crack easily.

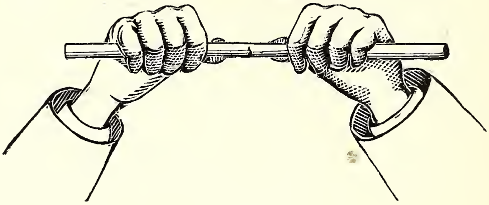


FIG 17.

Bending Glass.—A flame is required that will cover a large surface of glass, and the ordinary fish-tail and bat's-wing flames are the best for this purpose; of the two the fish-tail is preferable. Never attempt to bend glass tubing in a Bunsen flame, as it is next to impossible to do it properly. To bend a piece of tubing, you hold it with one hand on each side of the particular part you wish to operate upon, and then place the part near the top of the fish-tail flame, and gently rotate the tube in order to heat it uniformly over a space of two or three inches (Fig. 18). After a time you will feel the glass soften; then take it

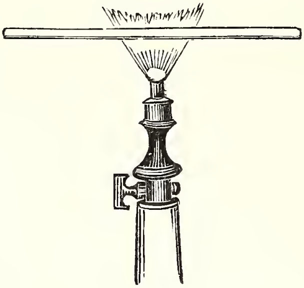


FIG. 18.

out of the flame and bend it to the desired angle. The glass will now be covered with a layer of soot; allow it to cool with the soot on it, so as to anneal the glass; that is, prevent any strains being set up by unequal cooling. Lastly, round off the two rough ends of the tube by heating them in the Bunsen flame.

To Draw Out a Glass Jet.—For this purpose a blow-pipe flame is required, although if the glass is thin it may be done in a Bunsen flame. The glass is held in both hands and a blow-pipe flame is caused to impinge on the part to be drawn out. Rotate the glass until soft, then take it out of the flame and pull gently, not suddenly; you will then have two pieces of glass joined by a fine capillary tube (Fig. 19). Cut the fine tube at the part required and just melt the edges in the flame, and anneal by placing in a crucible of dry sand, which allows the glass to cool slowly. All glass should be annealed after heating; if this is not done it will generally be found to crack on cooling; and unannealed glass also flies to pieces when heated.

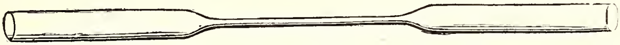


Fig. 19.

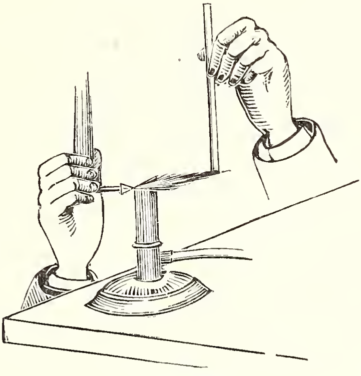


Fig. 20.

To Seal or Close Glass Tubing.—Proceed precisely as if you were going to draw out a jet; then heat the capillary tube at the part nearest the glass, and draw out; rotate the sealed end in the blow-pipe flame until soft (Fig. 20), and then blow very gently down the tube until the glass at the end is properly rounded; anneal thoroughly afterwards.

A piece of glass tubing about twelve inches long, sealed up at both ends, will be found useful as a stirring rod for stirring up solutions. It is not so liable to go through the bottom of a glass beaker as the same length of glass rod.

CHAPTER VI.

PREPARATION OF GASES.

As an introduction to the study of practical chemistry, the beginner cannot do better than endeavor to prepare the elementary gaseous bodies—hydrogen, nitrogen and oxygen—and study their properties when in the free or uncombined state. He will thereby learn lessons in manipulation which will be available to him in all photographic processes.

OXYGEN.

Symbol, O. Atomic weight 16.

Oxygen exists free in the atmosphere, but it is there mixed with about four times as much of nitrogen; the composition (by bulk) of pure air being—

Oxygen	21
Nitrogen	79
	100

Oxygen was first obtained by itself in 1774, by Dr. Priestley. He heated some red precipitate (oxide of mercury, HgO) in a glass tube and noted that this substance was decomposed into a gas (oxygen), which issued from the tube, while metallic mercury remained behind (Fig 21).

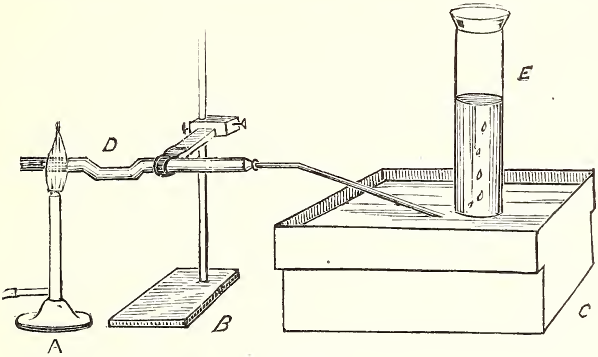


FIG. 21.

$$HgO = Hg + O.$$

The gas so prepared was found to possess many remarkable properties. It was named *oxygen* (*i.e.*, producer of sour things) by the great French chemist Lavoisier, because he believed it to be a necessary part of all acids.

Oxygen is most conveniently prepared by intimately mixing together five parts, by weight, of potassium chlorate with one part of black oxide of manganese. Each pound of the chlorate will produce nearly four cubic feet of oxygen. As an experiment, place a couple of ounces of the mixture in a thin glass flask (Florence flasks, in which oil is imported, answer very well), fitted with a cork and delivery tube, the other end of which dips under the water in a pneumatic trough. Heat the flask gently and oxygen gas will be given off in abundance. It may be collected by placing the end of the delivery tube underneath the mouths of bottles or cylinders filled with water, and inverted in the trough.

$$\underset{\text{Potassium Chlorate}}{KClO_3} = \underset{\text{Potassium Chloride}}{KCl.} + \underset{\text{Oxygen.}}{{}_3,O.}$$

The potassium chloride remains in the flask mixed with the black oxide of manganese, which itself undergoes no change (Fig. 22).

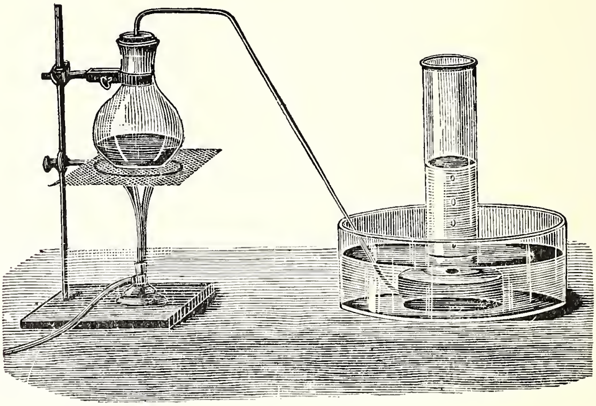


FIG. 22.

Oxygen gas is colorless, tasteless, transparent and inodorous. It combines eagerly with nearly all the other elements, the process of combination being known as oxidation. It is the oxygen in the air which sustains the burning of all our candles, fires, and gas-jets, for, although itself incombustible, it is the great supporter of combustion. Substances which burn in the air burn far more brilliantly in pure oxygen. Thus, if a piece of charcoal (which only smoulders away in the air) be fastened by wire to an iron rod, heated and introduced into a bottle full of oxygen it blazes up and emits showers of sparks. The result of this combination is the formation of an oxide of carbon commonly known as carbonic acid gas.

$$C \quad + \quad O_2 \quad = \quad CO_2$$

Carbon *unites with* Oxygen *to form* Carbonic Acid Gas.

The metal magnesium has a great affinity for oxygen, and when burned in a large vessel of the gas gives a flame of dazzling brilliancy.

$$Mg \quad + \quad O \quad = \quad MgO.$$

Magnesium *combines with* Oxygen *to form* Oxide of Magnesium.

Or we may mix the powdered metal with some substance rich in oxygen, as chlorate of potash, gun-cotton, etc. The mixture will burn almost instantaneously when a light is applied, and this "flash-light" is now largely used in winter for taking portraits, etc.

Oxygen is the most abundant of all the elements. It forms (by weight) more than one-fifth of the atmosphere, eight-ninths of water, and one-half of the rocks which compose the crust of the Earth.

Several plans have been devised for obtaining oxygen from steam, or from the atmosphere. Ten or twelve years ago Tessié du Motay used manganate of soda, which absorbed oxygen when a current of superheated steam was passed over it, and became converted into permanganate. The latter substance was then strongly heated, when it gave up its absorbed oxygen, returning to the state of manganate, which could be used over and over again.

This method, however, did not prove the commercial success which was expected.

In 1886 M. Brins commenced working on a large scale a method of extracting oxygen from the air by heating barium oxide (BaO) in retorts. At a temperature of about 900 deg. Fahr. this substance absorbs oxygen and is converted into barium peroxide (BaO_2). But when the heat is raised to 1400 deg. Fahr. the peroxide is decomposed as follows:

$$BaO_2 \quad = \quad BaO \quad + \quad O.$$

Barium peroxide *yields* barium oxide *and* oxygen.

Oxygen gas prepared by this process, and compressed into steel cylinders, is now sold in London at fourpence per cubic foot.

HYDROGEN.

Symbol, H. Atomic weight, 1.

Hydrogen gas is the lightest of all known substances, and hence is frequently used for filling balloons. Hydrogen is colorless, tasteless, transparent and without smell. In these properties it resembles oxygen; but it differs from that element in being highly inflammable, burning with a pale blue flame. The most abundant source of hydrogen is water, of which it forms one-ninth by weight; but it is also an ingredient of many other substances.

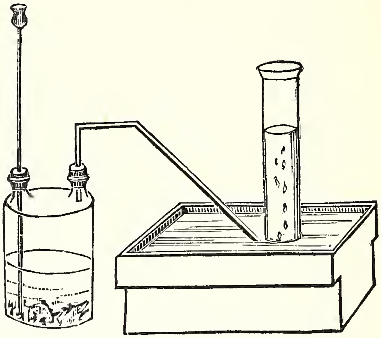


FIG. 23.

Hydrogen gas is most conveniently prepared from sulphuric acid by acting upon it with zinc (Fig. 23). Cut the zinc into small pieces and place them in a Woulff's two-necked bottle fitted with a thistle-funnel and a delivery-tube. Dilute the sulphuric acid with eight times its weight of water and pour it upon the zinc. A violent bubbling is seen, and hydrogen gas escapes through the delivery-tube. It may be collected in bottles over the pneumatic trough.

$$H_2SO_4 \quad + \quad Zn \quad = \quad ZnSO_4 \quad + \quad H_2$$
Sulphuric Acid *and* Zinc *produce* Sulphate of Zinc *and* Hydrogen.

A mixture of hydrogen and air (and especially of hydrogen and oxygen) is explosive; and in lantern entertainments where the "mixed gases" were used, many serious accidents have been caused by the violent combination of the two elements.

Hydrogen appears to have been known to the alchemist Paracelsus, in the sixteenth century; but its properties were first scientifically studied by Cavendish in 1781.

NITROGEN.

Symbol, N. Atomic weight, 14.

Nitrogen resembles both oxygen and hydrogen in being colorless, transparent, tasteless and inodorous. But it differs from oxygen in not being a supporter of combustion (a lighted candle goes out immediately when placed in a bottle of nitrogen gas), and from hydrogen in not being inflammable.

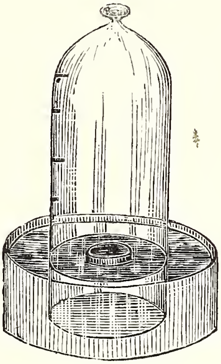


FIG. 24.

Nitrogen exists free in the air, of which it forms nearly four-fifths; combined with other substances it occurs in the bodies of animals and plants, and it is also an ingredient of many chemical compounds—ammonia (NH_3) for example.

Nitrogen is readily obtained from the air by removing the oxygen with which it is mixed.

Place a small piece of dried phosphorus in a little porcelain crucible floating on the water in a pneumatic trough; place a bell-jar over the saucer, and ignite the phosphorus by touching it with a hot wire, putting in the stopper of the jar immediately the wire is removed. The phosphorus burns vigorously, combining with the oxygen to form dense white fumes, which are oxide of phosphorus (Fig. 24). These fumes dissolve in the water under the bell-jar, and we thus remove all the oxygen from the air within the jar, the water rising up one-fifth the height of the jar to take its place, showing that oxygen forms one-fifth of the atmosphere; the remaining gas is nitrogen. Introduce a lighted candle into the bell-jar and it at once ceases to burn. Nitrogen is a very inert element, not combining readily with the other elements. In conjunction with hydrogen and oxygen, however, it forms a powerful acid, *Nitric Acid* (HNO_3).

Until the last month of the year 1877, the gaseous elements Oxygen, Hydrogen and Nitrogen were known as the *permanent gases;* because they never had been liquefied—much less solidified. But in that year the Continental experimentalists Cailletet and Pictet succeeded—by using great cold and tremendous pressure—in reducing all of these substances first to the liquid and then to the solid state.

CHAPTER VII.

BOOKS, APPARATUS, CHEMICALS.

Chemistry is a very wide subject, and those who wish to study it fully will find the following books very useful.

I. As a general introduction to the science, "Roscoe's Lessons in Elementary Chemistry," published by Macmillan, 4*s*. 6*d*.; Sexton's Stockhardt and Heaton's "Principles of Chemistry," Bell, 5*s*.; Thorpe's "Inorganic Chemistry," 2 vols., Collins, 6*s*.; Fowne's and Watts' "Chemistry," Vol. I., Inorganic, 9*s*.; Vol. II., Organic, 10*s*., Churchill.

II. Books treating of the qualitative analysis of substances; *i.e.*, that branch of chemistry which tells us how to discover simply of what chemical elements any given substance is composed: Thorpe and Muir's "Manual of Qualitative Analysis," Longmans, 3*s*. 6*d*.; Clowes' "Qualitative Inorganic Analysis," Churchill, 7*s*. 6*d*.

III. Books treating of quantitative analysis, by which we determine not only of what elements any given substance is composed, but also how much, by weight, of each element is contained in it: Thorpe's "Quantitative Analysis," Longmans, 4*s*. 6*d*.; Fresenius' "Quantitative Analysis," Vol. I. Churchill, 15*s*.

IV. Books of reference*: "Chemistry," by Roscoe and Schorlemmer, six vols., 18*s*. and 21*s*. each, Macmillan; Watts' "Dictionary of Chemistry," nine vols., £15 2*s*. 6*d*., Longmans (a new edition of this most valuable book is now appearing).

V. There are also several books dealing with the theories upon which our modern chemistry is based, which the student will find deeply interesting: Cooke's "The New Chemistry," Kegan Paul, 5*s*.; Tilden's "Chemical Philosophy," Longmans, 3*s*. 6*d*.; Muir's "Principles of Chemistry," Cambridge

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*The Appendix, by Professor Ehrmann, to the recently published "Photographic Instructor," is a valuable work of reference on the nature and use of the various chemicals and substances employed in photographic practice.—*Editor* PHOTOGRAPHIC TIMES.

Press, 15*s.*; Meyer's "Modern Theories of Chemistry," Longmans, 18*s.*

CHEMICAL APPARATUS

Chemistry learned from books alone is all but valueless. True chemistry is, above all things, an experimental, observational and inductive science. The apparatus and chemicals contained in the following lists will enable any one to go through the ordinary practical course in chemistry as laid down in the text-books, and to conduct qualitative analyses. For quantitative analysis, a delicate balance in glass case (Fig. 45) will be the principal additional article required.

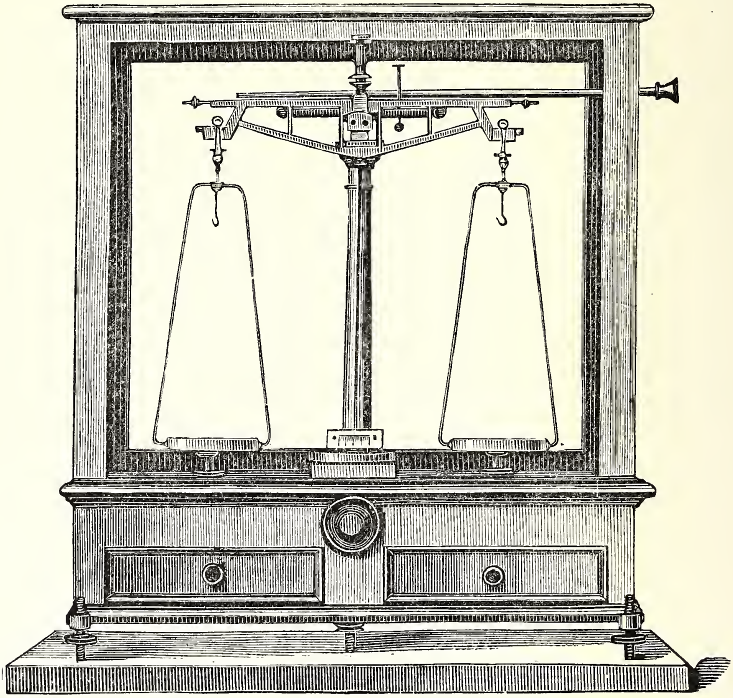


FIG. 45.

LIST OF CHEMICAL APPARATUS.

2 hard glass flasks, fitted with safety thistle funnels and leading-tubes, arranged for the preparation of hydrogen, carbonic acid, chlorine gases, etc. (Fig. 25.)

2 hard glass flasks, with leading-tubes, for the preparation of oxygen, laughing-gas, etc.

1 flask-holder, for the hand.

Sheet-iron retort, for oxygen.

Japanned tin pneumatic trough, with side-shelves. (Fig 26.)

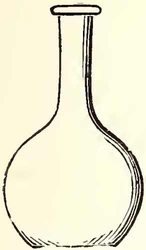


Fig. 25.

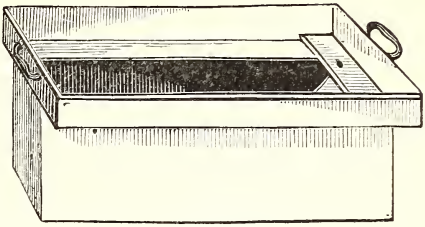


Fig. 26.

Metal spirit-lamp with double wick, and ring to support flasks, or, where gas is obtainable, a Bunsen's gas-lamp instead of the spirit-lamp.

1 iron tripod, with sand-bath dish, (Fig. 27.)

1 gas receiver, capacity one pint, fitted with brass cap, stop-cock, bladder and ferrule, and brass jet for burning hydrogen.

3 gas receivers, one quart capacity, one plain and two stoppered.

2 earthenware trays for removing gas receivers from pneumatic trough when filled.

3 ground-glass plate covers, for gas receivers.

Deflagrating jar, one pint capacity, with ground edge, brass cap and spoon for phosphorus, sulphur, etc.

1 taper-holder.

Strong glass tube, for exploding the mixture of hydrogen and oxygen.

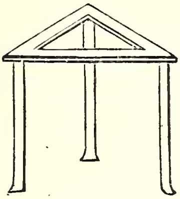


Fig 27.

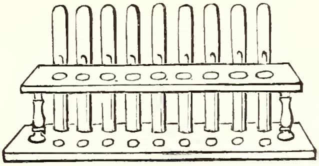


Fig. 28.

2 goldbeaters skin balloons for hydrogen,

Mouthpiece, for inhaling laughing-gas from a bladder or gas-bag.

Conical brass blow-pipe.

6 in. platinum wire.

Piece 2 in. x 1 in. platinum foil.

1 test-tube stand, 24 holes. (Fig 28.)

36 test-tubes, 6-in. x $\frac{3}{4}$-in.
24 " 5-in. x $\frac{1}{2}$-in.
1 test-tube basket.
1 " " holder. (Fig 29.)
2 boiling-tubes.
5 test-tube brushes.
1 set of 5 spouted beakers.
1 each Bohemian flasks, 2-oz., 4-oz., 8-oz., 16-oz., and 30-oz.
1 each Berlin crucibles, $1\frac{1}{4}$-in. and $1\frac{1}{2}$-in.
1 " " basins, $2\frac{7}{8}$-in., $3\frac{1}{2}$-in. and 4-in.
1 " " funnels, $1\frac{1}{2}$-in. and 2-in.
3 glass funnels $2\frac{1}{2}$-inch.
1 glass funnel, 3-inch.
1 black-wood funnel stand.
2 quires filter paper.
1 set of 4-filter cutters.
1 tripod stand, 5-in.
Iron retort stand, with 3 rings. (Fig. 30.)

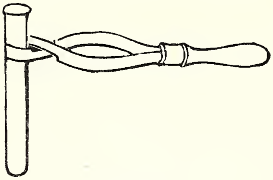
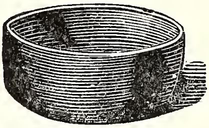


FIG. 29.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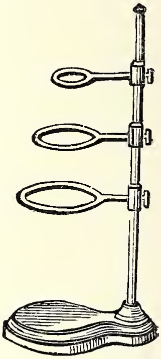
FIG. 30.

2 pieces iron gauze, 5-in. square.
1 sand-bath, 5-in. (Fig 31.)
6 watch-glasses, 3-in. diam.
2 lbs. glass tube.
1 lb. " rod.
$\frac{1}{2}$ lb. combustion tube.
6 feet black india-rubber tube $\frac{3}{8}$-in.
2 " " " " $\frac{1}{8}$-in.

2 acid-funnels, 18-in. (Fig. 32.)
6 dozen assorted corks.
2 Woulffe's bottles, 20-oz., two necks.
1 stoppered retort, 2-oz. (Fig. 33.)
1 set of 3 cork-borers.
1 triangular file, 4-in.
1 round " 5 "
1 square-flat " 8 "

1 Bunsen's burner, with blow-pipe jet, star support and chimney.
1 rose burner for same.
1 pair brass crucible tongs, 8-in. (Fig. 34
1 porcelain mortar, 4-in., and pestle.
1 steel spatula, 5-in. (Fig. 35)
6 boxes litmus test-papers.

2 deflagrating spoons. (Fig. 36.)
Wash-bottle. (Fig. 37.)
1 thermometer, enameled, 300° Cent.
1 each stoppered flasks, graduated to deliver 250, 500 and 1,000 c.c.
1 each pipettes, graduated to deliver 25, 50 and 100 c.c.
1 pipette, 10 c.c. graduated in $\frac{1}{10}$.

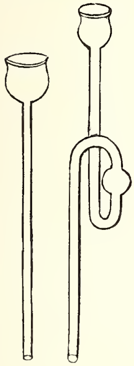
Fig. 32.

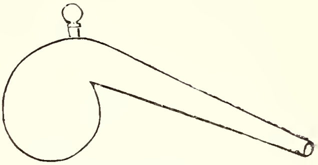
Fig. 33.

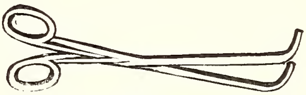
Fig. 34.

1 pair watch-glasses and clip.
1 small stoppered weighing-bottle.
1 tile, 6-in., glazed both sides.

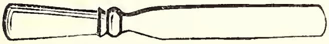
Fig. 35.

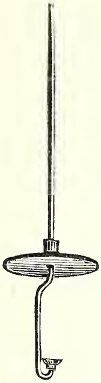
Fig. 36.

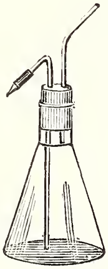
Fig. 37.

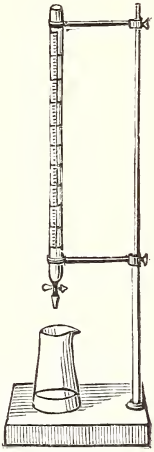
Fig. 38.

1 packet Swedish filter paper, $4\frac{1}{2}$-in.
2 Berlin crucibles and covers.
1 Geissler burette, 100 c.c. in $\frac{1}{5}$. (Fig. 38.)

1 stand for same.
6 beakers, 20-oz., and covers.

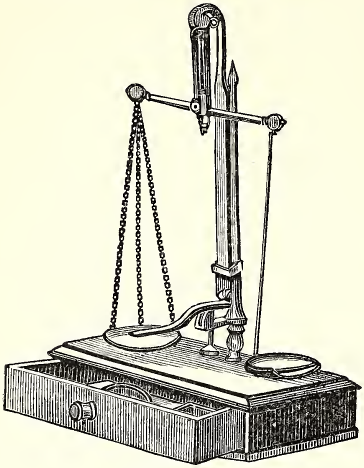

Fig. 39.

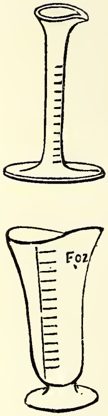

Fig. 40.

1 glass desiccator.
1 pair of small scales with weights, to pack in box. (Fig. 39.)

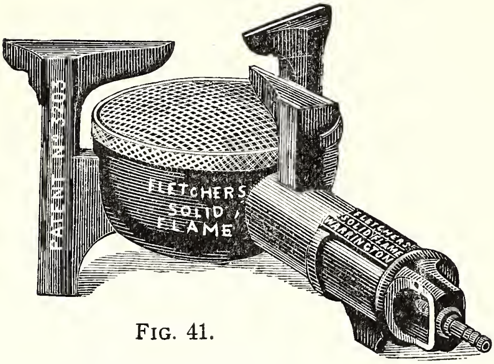
PATENT No 3705
FLETCHERS SOLID FLAME
FLETCHER'S SOLID FLAME WARRINGTON

Fig. 41.

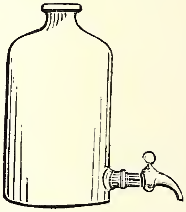

Fig. 42.

2 graduated glass-measures (Fig. 40). 1 solid-flame gas-burner (Fig. 41).
1 glass jar, with stop-cock, to hold distilled water, etc. (Fig. 42.)

Chemicals.

1 lb. acid hydrochloric, pure.
1 lb. " " com'l.
1 lb " nitric, pure.
1 lb. " sulphuric, com'l.

$\frac{1}{4}$ oz. cadmium metal.
$\frac{1}{4}$ oz. cobalt nitrate.
$\frac{1}{4}$ oz. manganese sulphate.
1 oz. microcosmic salt.

1 lb. acid, sulphuric, pure.
2 oz. 〃 oxalic.
1 lb. ammonia .880.
4 oz. ammonium chloride.
2 oz. 〃 nitrate.
½ lb. iron sulphide.
2 oz. asbestos, picked.
2 oz. barium chloride.
4 oz. calcium chloride, dried.
½ lb. wood charcoal.
½ lb. copper turnings.
4 oz. iron filings.
1 oz. lead acetate.
1 oz. litmus.
2 oz. magnesium sulphate.
1 lb. manganese binoxide.
½ lb. marble.
1 oz. plaster of Paris.
½ oz. phosphorus.
2 oz. potassium bichromate, pure.
2 oz. 〃 chlorate.
4 oz. 〃 nitrate.
2 oz. 〃 ferrocyanide.
2 oz. 〃 ferricyanide.
4 oz. glycerine.
4 oz. fluor spar.
¼ oz. silver nitrate.
1 lb. caustic soda.
¼ oz. sodium metal.
4 oz. sodium acetate.
1 pint methylated spirit.
½ lb. sulphur, roll.
½ lb. zinc, granulated.
3 packets of labels.
2 oz. acid arsenious.
½ oz ammonium phosphate.
2 oz. 〃 oxalate, pure.
½ oz. bismuth, metal.
2 oz. borax.
2 oz. tartaric acid, cryst.
¼ oz. nickel sulphate.
1 oz. potash alum.
½ oz. strontium nitrate.
4 oz. zinc, purified.
1 lb. acid, acetic.
1 oz. 〃 boracic.
¼ oz. 〃 molybdic.
2 oz. ammonium chloride, pure.
1 lb. 〃 sulphide.
2 oz. 〃 carbonate.
1 oz. barium hydrate.
1 oz. chloroform.
4 oz. ether, sulphuric, methylated.
½ oz. potassium bromide.
½ oz. 〃 iodide.
2 oz. sodium carbonate, dry, pure.
2 oz. 〃 phosphate.
1 oz. copper sulphate.
1 oz. Iceland spar.
2 oz. iodine, resublimed.
1 oz. pure iron (piano-forte) wire.
½ oz. mercury chloride.
½ oz. lead nitrate.
1 oz. potassium chromate.
1 oz. 〃 permanganate.
1 oz. 〃 sulphate.
2 oz. sodium chloride.
4 oz. 〃 hyposulphite.
1 oz. tin, granulated.
1 oz. uranium nitrate.
¼ oz. zinc sulphate.
1 lb. copper turnings.
2 oz. ferric chloride.
1 lb. paraffine wax.
¼ lb. starch.
1 lb. calcium oxide (quicklime).
½ pint alcohol.
1 quart methylated spirit.

If the student lives at a distance from any reliable dealer, it will be well to lay in duplicates of all the glass apparatus, and four times the weight of each chemical named above. In the absence of a gas supply a couple of spirit-lamps and half a gallon of methylated spirit will be required as a substitute.

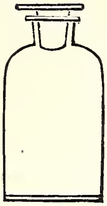

Fig. 43.

Chemicals in the solid state should be kept in wide-mouthed corked (or, better, stoppered) bottles. Chemicals in the liquid state should be kept in narrow-mouthed bottles (Fig. 43) having ground-glass stoppers (the stoppers should be lubricated with a little vaseline). Acids, alcohol, ether, and ammonia should especially never be kept in corked bottles.

All chemicals should be kept in a cupboard, under lock and key. Many of them are dangerous poisons, and numerous fatal accidents have occurred through their being carelessly kept. Every bottle should be distinctly labeled, and the label coated first with size and then with thin varnish.

CHAPTER VIII.

TREATMENT OF RESIDUES.

Why Residues Should be Collected.—Certain of the substances used by the photographer—the compounds of gold and silver for example—are very costly; and it is fortunate that for the production of each picture only a very small quantity of these valuable articles is required. But although the amount of these precious metals actually retained in each negative or print is very small, yet for the perfect production of the picture it is necessary that there should be present—at the commencement of the operation—a much larger quantity. Now, with many photographers, the proportion not used—the residue—goes down the sink and is lost. This is a pity, because it is an easy thing to recover the valuable portion of such residues, and thereby to make photography more profitable to the professional and a less expensive recreation to the amateur, while the task of recovery will teach more than one lesson of value.

Residues to be Preserved.—Of the various reagents employed by the photographer, five at least are of sufficient value to require their collection and preservation with a view to subsequent treatment. These are: (1) The salts of gold; (2) the salts of silver; (3) salts of platinum; (4) alcohol, and (5) potassium oxalate.

HOW TO COLLECT RESIDUES.

Certain vessels must be set aside—one for each residue—so that six or seven receptacles will be wanted altogether. The best shape is conical, as the solid matter then sinks more rapidly to the bottom, not having the same chance of adhering to the sides. A plug, or tap of some kind, should be placed near the bottom of each vessel, so that the clear liquid above can be drawn off from time to time.

For the gold residue a glass vessel is best, while earthenware answers for the silver; even casks, tarred inside, are used by many. Every solution should be emptied into its proper vessel immediately it is done with, and the dish which contained it washed out. It is comparatively easy to clean a dish or vessel just after use, but when the dregs are allowed to dry, they are far more difficult to remove.

Recovery of Gold from Residues.

Gold residues—the spent toning-baths—should be collected in conical glass precipitating-jars. Such jars can be obtained of any size up to a gallon, and the size of jar to be employed must, of course, be regulated by the extent of the photographer's operations. Although the bath may refuse to tone any more prints, yet it still contains a considerable percentage of the amount of gold which was added to it to commence with, and also a larger amount of silver chloride, washed off the as yet unfixed prints which have been soaked in it.

When the gold residue jar is nearly full, add a little sulphuric, and then a rather larger quantity of hydrochloric acid—say an ounce of the two to a quart of solution. Now stir in gradually a saturated solution of ferrous sulphate, until it ceases to produce the least precipitate. A black deposit is formed, which consists of metallic gold mixed with carbonate and oxide of iron. This precipitate is in such a fine state of division that it sinks very very slowly and must be allowed a couple of days to go to the bottom.

Now very carefully pour away—or syphon off—the supernatant clear liquid and collect and dry the residue. In all ordinary cases it is better to keep all residues of gold and silver until they have reached a certain bulk, and then send them to a respectable refiner, who will extract the precious metals with far greater certainty and less expense than any individual not in that special trade. For this purpose it is only necessary to scrape out the moist residue with a spoon, place it in a porcelain dish or crucible—or in one of the enameled iron dishes now so common—and dry it in an oven.

Reduction of Gold Residues.

If the photographer, however, wishes to see for himself how much gold he can actually extract, he must add water acidulated with sulphuric acid to the residue, and stir it up well, then allow to settle, and repeat the process ; and, lastly, wash it well twice with pure water. Lastly, let the residue be dried and placed in a little "assay pot" lined with borax, along with some fusion mixture. The pot must be strongly heated in a furnace, when a button of mixed gold and silver will be found at the bottom. Add to this button three times its weight of silver, melt the whole in a plumbago crucible, and pour the liquid metal into cold water. Dissolve the granulated metal in warm dilute nitric acid, when the silver will be removed in the form of nitrate, and the gold will be left as a brown powder, which may then be converted into chloride.

Recovery of Silver from Residues.

The "silver waste" is derived from at least three sources, and the waste from each source had better be treated separately.

First we have the *trimmings of the sensitive paper.*

It is always best to trim the prints before toning, as no gold is then used up in toning the margins, and, moreover, the prints are less likely to tear in the subsequent washing. All such trimmings should be kept in a dry box or basket. Then there are filter papers, through which solutions of silver have been passed, and the bits of blotting paper used to absorb the drainings from sensitized paper ; all these should be dried and added to the rest.

When the receptacle for paper is full the contents must be burned—a handful at a time—on a large iron tray placed on three or four bricks. Each pound of paper cuttings should yield about an ounce of drab-colored ash. An ordinary fire grate may be used for the burning if it is first carefully cleaned out. The paper should be lighted *at the top*, and fresh paper added little by little ; otherwise the strong draught may carry part of the fine ashes up the chimney.

Next comes an important source of silver—the *wash-water* *from silver prints.* Every one knows how milky the first two or three waters appear in which prints are washed before toning. This milkiness is due to chloride of silver washed out of the paper; and it is certain that many thousand dollars' worth of silver are in this way literally thrown away every year.

The first three—or even the first six—wash-waters should be placed in a large earthenware vessel or tarred tub, and with each a little commercial hydrochloric acid must be added, which will rapidly precipitate the silver chloride, causing it to settle at the bottom as a white mud. Many workers add common salt instead of the acid, and this answers fairly well; the objection to it is that silver chloride is soluble in a strong solution of common salt, and as this substance is so cheap, too much of it is frequently added, the result being that some of the silver is poured away in solution. Before the clear liquid is thrown away a drop of hydrochloric acid, or a solution of common salt should be added to a glassful of the liquid; if any cloudiness then appears it shows that the whole of the silver chloride has not been precipitated. As the vessel fills, the clear upper portion may be drawn off from time to time by a tap or syphon, or by simply lading it out or pouring it off. When the deposit at the bottom has reached a considerable amount, all the liquid should be poured off and the deposit stirred up with clean water. Lastly, pour the water away and remove the residue with a spoon, placing it in a dish in the oven to dry.

Another source of silver is in the *old hyposulphite of soda fixing-baths*, both of negatives and prints. These should be poured as they are done with into a separate vessel. They contain silver in the form of a double salt—the hyposulphite of silver and sodium. If several strips of zinc are kept hanging in the vessel much of the silver will be deposited on the zinc through the electrical action which is set up. This silver adheres loosely to the zinc as a dark powder, and may readily be brushed off. To secure the remainder of the silver in the solution, some liver-of-sulphur (potassium sulphide) should be added, which will precipitate the silver as black silver sulphide.

The latter operation should be conducted in the open air, as offensive fumes of sulphuretted hydrogen are given off. The black silver sulphide may be scraped out, dried and sent to the refiner; or it may be reduced by heating to a red heat in a fire-clay crucible with saltpetre on a clear fire. The contents of the crucible are removed, washed with water and filtered, when the pure silver is left on the filter. It can then be dissolved in nitric acid to form silver nitrate.

Another residue which contains silver is spoiled gelatine emulsion—which may be boiled with a little sulphuric acid so as to be rendered incapable of setting, and added to the hypo residue.

A neat method for the recovery of metallic silver from silver chloride is to melt the chloride in a porcelain dish over a Bunsen burner, and then to insert in the liquid one end of a piece of platinum wire about six inches in length. When the silver chloride cools it will hold this end of the wire firmly. Now attach the other end of the wire (by means of a binding screw) to a strip of amalgamated zinc and immerse the whole in a vessel of dilute hydrochloric acid.

After a few minutes the mass of silver chloride will be seen to become streaked with gray porous metallic silver, and in a few hours the whole of the chloride will be reduced. The spongy mass of silver remaining can now easily be detached from the porcelain dish, and must be washed to free it from acid, and then dried. To obtain the silver as a button of bright metal the grayish mass must be fused before the blowpipe in a bone-ash cupel with a little lead until the latter metal becomes oxidized and is absorbed by the cupel, leaving pure silver behind.

Recovery of Silver in the Wet Way.—Another method of obtaining silver from silver chloride is to decompose the salt by electricity. The residue containing the silver chloride may be placed in any large-mouthed earthenware vessel, in the centre of which must be placed a porous cell such as is generally employed in the construction of galvanic batteries. The porous cell must be filled with water acidulated with a little sulphuric acid, and in it must be placed a rod of zinc which has been amalgamated (coated with mercury); a copper wire is soldered to the zinc, and to the other end of the wire a silver plate (a large spoon will do) is attached, and this is made to dip into the silver solution. An electric current is immediately produced, and the metallic silver slowly settles upon the silver plate, which may then be taken out and the particles of silver rubbed off and well washed.

Results of Recovering the Residues of the Precious Metals.

One of our leading photographers—Mr. Valentine, of Dundee—lately published the results which he obtained from the collection of the gold and silver residues employed in his extensive business. In a given time he used £694 10s. 0d. worth of nitrate of silver. Of this he received from the refiner as the value of the ashes of sensitized paper, £104 0s. 3d.; the residues obtained from the washing of prints were worth £178 10s. 3d.; and the value of the old hyposulphite of soda fixing-baths £193 16s. 4d. Thus the value of the silver residues was £476 7s. 3d., so that *more than two-thirds* of the silver employed was actually recovered.

Of gold used to the value of £274, there was recovered from the spent toning-baths £101 14s. 3d. The refiner's charge, for reducing both gold and silver to the metallic state, was £24 10s. 9d., and Mr. Valentine adds, "I have never been able to do it so cheaply myself."

From these considerations, it is evident that care in looking after residues may make a considerable difference in the profits of a large business.

Platinum Residues.

Metallic platinum is worth about half as much as gold, so that workers of the platinotype process will find it worth their while to collect all their platinum residues. The solution with which the Platinotype Company coat their paper contains about sixty grains of platinum salt to the ounce; and as only one-tenth of the metallic platinum present is used in forming the picture, it is evident that the remaining nine-tenths is left for collection by the careful worker. When the used baths amount to a quart or two they should be heated in a large beaker over a sand-bath to near the boiling point, and a saturated solution of ferrous-sulphate added at the rate of half a pint to each quart of the residue. This will precipitate the platinum as a black powder, which will speedily sink to the bottom, and may be collected, washed and dried. The liquid remaining is ferrous-oxalate, and may be added to the oxalate residues.

Another method is to evaporate all the platinum residues to dryness. Burn the paper, and mix all the ashes, etc., in a clay crucible with fusion mixture, and heat strongly. After half an hour spongy platinum will be formed. Wash this well with water, and dissolve it in *aqua-regia* (three parts HCl to one of HNO_3). Evaporate the solution to dryness, add water, and then ammonium chloride. A yellow precipitate of the double chloride of platinum and ammonia is formed. Filter this off, wash it with methylated spirit, dry and ignite in a porcelain crucible, when pure metallic platinum will be obtained.

Oxalate Residues.

The comparatively high first cost of the ferrous-oxalate developer is sometimes urged as an argument against its use, the cost of the neutral potassium-oxalate which is employed in making it being thirty-two cents per pound. But if the used developer is preserved until a sufficient quantity has accumulated, it is not difficult to prepare the potassium-oxalate from it again at a nominal cost. The solution to be treated must be placed in a large glass vessel and potassium-carbonate gradually added until a precipitate ceases to be produced. By filtering, the powdered carbonate of iron which has been formed can be removed, and the filtrate should be perfectly clear. Oxalic acid must now be added to the filtrate until litmus paper shows that the solution is neutral, after which it can be evaporated down till crystals begin to appear. It is then a saturated solution of neutral potassium-oxalate, and is ready for use again.

ALCOHOL.

Although less alcohol is now used than formerly in the preparation of collodion, owing to the introduction of gelatine dry plates, yet, on the whole, a very much larger quantity is employed in photography, as it is now used in preparing and precipitating gelatine emulsion, for hardening and drying negatives, and in compounding certain developers.

For ordinary work it is sufficient to add potassium carbonate to the dilute alcohol. The potassium salt combines with the water and separates from the alcohol, which is left on top and can be syphoned off. By heating the potassium carbonate it can be freed from the water and is then ready for use once more.

If, however, it is necessary that the alcohol should be *pure*, as in that required for the manufacture of collodion, the above plan will not answer, and resort must be had to *distillation with quick-lime.*

CHAPTER IX.

TABLE OF CHEMICAL ELEMENTS AND COMPOUNDS COMMONLY EMPLOYED IN PHOTOGRAPHY.

NAME.	FORMULAS.	Molecular Weight	PRICE.
Acetic Acid.	$C_2H_4O_2$	60	$0 20 lb
Albumen.	$C_{72}H_{112}O_{18}N_{22}SP.$	..	1 00 lb
Asphaltum.	......	..	15 lb
Alcohol (Ethylic Alcohol).	C_2H_6O	46	40 lb
Aldehyde (Acetyl Aldehyde).	C_2H_4O	44	1 00 lb
Aluminium-Ammonium-Sulphate (Ammonia Alum).	$Al_2(SO_4)_3+(NH_4)_2SO_4+24OH_2$	906.8	10 lb
Aluminium Potassium-Sulphate (Common Potash Alum).	$Al_2(SO_4)_3+K_2SO_4+24OH_2$	768	10 lb
Aluminic Nitrate.	$Al_2(NO_3)_6+16OH_2$	326	2 00 lb
Aluminic Sulphate.	$Al_2(SO_4)_3+18OH_2$	666	10 lb
Ammonia.	NH_3	17	...
Ammonium.	NH_4	18	....
〃 Hydrate.	NH_4HO	35	15 lb
〃 Bichromate.	$(NH_4)_2Cr_2O_7$	252	1 50 lb
〃 Bromide.	NH_4Br	98	65 lb
〃 Chloride.	NH_4Cl	53½	12 lb
〃 Iodide.	NH_4I	145	40 oz
〃 Nitrate.	$(NH_4)NO_3$	80	30 lb
〃 Sulphydrate.	$(NH_4)HS$	51	45 lb
Arsenic Bromide.	$AsBr_3$	315	65 oz
Barium.	$Ba.$	137	4 00 grm
〃 Chloride.	$BaCl_2+2OH_2$	345	24 lb
〃 Nitrate.	$Ba(NO_3)_2$	261	15 lb
Benzole (or Benzine).	C_6H_6	78	20 lb
Cadmium.	Cd	112	20 oz
〃 Bromide.	$CdBr_2+4H_2O$	344	26 oz
〃 Iodide.	CdI_2	366	50 oz
Calcium Bromide.	$CaBr_2$	200	15 oz
〃 Chloride.	$CaCl_2+6H_2O$	219	10 lb
〃 Iodide.	CaI_2	294	50 oz
Camphor.	$C_{10}H_{16}O$	152	35 lb
Canada Balsam.	......	..	45 lb
Caoutchouc.	......	..	2 50 lb
Carbolic Acid (Phenol).	C_6H_6O	94	50 lb
Carbonic Acid Gas.	CO_2	44	50 lb
Castor Oil.	.....	..	30 lb
Chloroform.	$CHCl_3$	119½	60 lb
Chlorinated Lime (Bleaching Powder or Calcium Hypochlorite).	$Ca(OCl)Cl$	127	10 lb

TABLE OF CHEMICAL ELEMENTS, ETC.—*Continued.*

NAME.	FORMULAS.	Molecular Weight	PRICE.
Chromium Potassium Sulphate.	$Cr_2(SO_4)_3,K_2SO_4+24H_2O$	998	....
Citric Acid.	$C_6H_8O_7+H_2O$	210	$0 75 lb
Collodion.	......	..	1 50 lb
Copper Sub-Bromide.	CuBr	143	....
〃 Bromide.	$CuBr_2$	223	60 oz
〃 Nitrate.	$Cu(NO_3)_2+3H_2O$	241	65 lb
〃 Sulphate.	$CuSO_4+5H_2O$	249	10 lb
Cyanogen.	C_2N_2(or Cy_2)	52	....
Ether (Sulphuric Ether).	$C_4H_{10}O$	74	75 lb
〃 Methylated.	....	..	....
〃 Methylic.	C_2H_6O	46	....
Formic Acid.	CH_2O_2	46	1 50 lb
Gallic Acid.	$C_7H_6O_5$	170	1 40 lb
Gelatine.	......	..	2 00 lb
Glycerine.	$C_3H_8O_3$	92	25 lb
Gold.	Au	196	50 grm
〃 Cyanide.	Au (CN)	222	2 50 grm
〃 Sodium Chloride.	$NaAuCl_4+2H_2O$	397	30 grm
〃 Trichloride.	$AuCl_3$	302½	14 00 oz
〃 Sodium Hyposulphite.	$AuNa_3S_4O_6+2H_2O$	525	....
Gum Arabic.	.....	..	80 lb
〃 Tragacanth.	......	..	50 lb
Hydriodic Acid.	HI	128	...
Hydrochloric Acid.	HCl	36½	10 lb
Hydrocyanic Acid (Prussic Acid).	HCN (or HCy)	27	1 00 lb
Hydrobromic Acid.	H Br	81	25 oz
Hydrofluoric Acid.	HF	20	2 00 lb
Hydrokinone.	$C_6H_6O_2$	110	1 00 oz
Hydrosulphuric Acid (Sulphuretted Hydrogen).	H_2S	34	50 oz
Hydroxyl.	H_2O_2	34	50 lb
Hydroxylamine.	NH_3O	33	....
Hydrochloride.	$NH_3(OH)Cl$	69½	....
Hypochlorous Acid.	HCl O	52½	....
Iridium Tetrachloride.	$IrCl_4$	335	1 25 grm
Iron Acetate.	$Fe(C_2H_3O_2)_2+4H_2O$	246	25 oz
〃 Ammonium Citrate.	.....	..	70 lb
〃 〃 Sulphate.	$FeSO_4(NH_4)_2SO_4+6H_2O$	392	14 lb
〃 Nitrate (*Ferric Nitrate*).	$Fe_2(NO_3)6$	484	....
〃 Oxalate (*Ferric Oxalate*).	$Fe_2(C_2O_4)_3$	376	1 50 lb
〃 Sulphate (*Ferric Sulphate*).	$Fe_2(SO_4)_3+9H_2O$	566	10 lb
〃 Bromide (*Ferrous Bromide*).	$FeBr_2+6H_2O$	324	25 oz
〃 Chloride (*Ferrous Chloride*).	$Fe\cdot Cl_2$	127	20 lb
〃 Iodide (*Ferrous Iodide*).	FeI_2+4H_2O	382	40 oz
〃 Nitrate (*Ferrous Nitrate*).	$Fe(NO_3)+6H_2O$	283	....
〃 Perchloride (*Ferric Chloride*).	Fe_2Cl_6	325	60 lb
〃 Protosulphate (*Ferrous Sulphate*	$FeSO_4+7H_2O$	278	10 lb

TABLE OF CHEMICAL ELEMENTS, ETC.—*Continued.*

NAME.	FORMULAS.	Molecular Weight	PRICE.
Kaolin (*China Clay*).	......	..	$0 10 lb
Lead Acetate (*Sugar of Lead*).	$Pb(C_2H_3O_2)2$	324	25 lb
" Chloride.	$PbCl_2$	242	75 lb
" Ferrocyanide.	$\left\{ \begin{array}{c} Pb_2Fe(CN)6 + \\ 3H_2O \end{array} \right\}$	678	20 oz
" Nitrate.	$Pb(NO_3)_2$	330½	20 lb
Lithium Bromide.	$LiBr$	87	40 oz
" Iodide.	$LiI + 3H_2O$	188	80 oz
Magnesium.	Mg	24	60 oz
" Bromide.	$MgBr_2$	184	50 lb
" Carbonate.	$MgCO_3$	84	35 lb
" Iodide.	MgI_2	278	72 oz
" Nitrate.	$Mg(NO_3)_2 + 6H_2O$	256	1 00 lb
" Sulphate.	$MgSO_4 + 7H_2O$	246	10 lb
Mercury.	Hg	200	80 lb
" Bichloride.	$HgCl_2$	271	75 lb
" Sub-chloride.	Hg_2Cl_2	471	....
" Monoxide.	HgO	216	....
Naphtha.	......	..	35 lb
Nitric Acid.	HNO_3	63	12 lb
Nitro-Hydrochloric Acid.	$HNO_3 + 3HCl$	..	....
Nitrous Acid.	HNO_2	47	20 lb
Oxalic Acid.	$C_2H_2O_4 + 2H_2O$	126	20 lb
Ozone.	O_3	48	....
Phosphoric Acid.	H_3PO_4	98	70 lb
Platinum.	Pt	194	9 00 oz
" Tetrachloride.	$PtCl_4 + 5H_2O$	426	5 00 oz
Potassium.	K	39	3 00 oz
" Bichromate.	$K_2Cr_2O_7$	294	15 lb
" Bromide.	KBr	119	45 lb
" Carbonate.	K_2CO_3	138	14 lb
" Chlorate.	$KClO_3$	122½	25 lb
" Chloride.	KCl	74½	40 lb
" Cyanide.	$K(CN)$(or KCy)	65	55 lb
" Ferricyanide.	K_3FeCy_6	329	80 lb
" Ferrocyanide.	$K_4FeCy_6 + 3H_2O$	422	30 lb
" Fluoride.	KF	58	2 00 lb
" Hydrate.	KHO	56	60 lb
" Iodide.	KI	166	30 oz
" Nitrate.	KNO_3	101	12 lb
" Nitrite.	KNO_2	85	75 lb
" Oxalate.	$K_2C_2O_4 + 5H_2O$	212	25 lb
" Permanganate.	$K_2Mn_2O_8$	316	30 lb
" Sulphate.	K_2SO_4	174	15 lb
" Silver Cyanide.	$KAg(CN)_2$	200	25 lb
" Sulphide.	K_2S	110	90 lb
" Sulpho-cyanide.	$KS(CN)$	97	1 15 lb
Prussian Blue.	$Fe_4(FeCy_6)_3$	860	60 lb
Pyrogallic Acid.	$C_6H_6O_3$	126	35 oz
Pyroxyline.	$C_{18}H_{22}(NO_2)_8O_{15}$	846	4 00 lb
Silver.	Ag	108	1 25 oz
" Acetate.	$C_2H_3AgO_2$	167	2 50 oz
" Ammonio-nitrate.	$AgNO_3 + 2NH_3$	204	....

TABLE OF CHEMICAL ELEMENTS, ETC.—*Continued.*

NAME.	FORMULAS.	Molecular Weight	PRICE.
Silver Bromide.	$AgBr$	188	$1 50 oz
" Carbonate.	Ag_2CO_3	276	3 70 oz
" Chloride.	$AgCl$	143½	1 35 oz
" Citrate.	$C_6H_5O_7Ag_3$	513	....
" Fluoride.	AgF	127	....
" Hyposulphite.	$Ag_2S_2O_3$	328	....
" Iodate.	$AgIO_3$	283	...
" Iodide.	AgI	235	1 75 oz
" Nitrate.	$AgNO_3$	170	75 oz
" Nitrite.	$AgNO_2$	154	2 50 oz
" Oxide.	Ag_2O	232	1 50 oz
" Sub-oxide.	Ag_4O	448	....
" Phosphate.	Ag_3PO_4	419	2 00 oz
" Sodium Hyposulphite.	$AgNaS_2O_3+2H_2O$	279	....
" Sulphate.	Ag_2SO_4	312	1 75 oz
" Sulphide.	Ag_2S	248	3 00 oz
Sodium.	Na	23	50 oz
" Acetate.	$NaC_2H_3O_2+3H_2O$	136	40 lb
" Bicarbonate.	$HNaCO_3$	84	10 lb
" Borate (Borax).	$Na_2B_4O_7+10H_2O$	382	15 lb
" Bromide.	$NaBr$	103	60 lb
" Carbonate.	$Na_2CO_3+10H_2O$	286	10 lb
" Chloride.	$NaCl$	58½	40 lb
" Hydrate.	$NaHO$	40	15 lb
" Hypochlorite.	$NaOCl$	74½	.....
" Hyposulphite.	$Na_2S_2O_3+5H_2O$	248	10 lb
" Iodide.	NaI	150	3 90 lb
" Nitrate.	$NaNO_3$	85	12 lb
" Silicate.	Na_2SiO_3	302	50 lb
" Sulphite.	$Na_2SO_3+7H_2O$	252	25 lb
" Tungstate.	$Na_2WO_42+H_2O$	330	35 lb
Starch.	$C_6H_{10}O_5$	162	15 lb
Strontium Chloride.	$SrCl_2+6H_2O$	266½	20 lb
Sugar (Sucrose).	$C_{12}H_{22}O_{11}$	342	....
Sulphuric Acid.	H_2SO_4	98	10 lb
Sulphurous Acid.	H_2SO_3	82	20 lb
Tannic Acid (Tannin).	$C_{14}H_{10}O_9$	322	1 45 lb
Tartaric Acid.	$C_4H_6O_6$	150	50 lb
Uranium Nitrate.	$UO_2(NO_3)_2+6H_2O$	504	75 oz
Vanadium.	V	51	22 00 grm
Water.	H_2O	18	15 gal
Zinc Bromide.	$ZnBr_2$	225	23 oz
" Chloride.	$ZnCl_2$	136	75 lb.
" Iodide.	ZnI_2	319	50 oz

The prices given above are those of a leading American firm.

CHAPTER X.

CHEMICALS EMPLOYED IN PHOTOGRAPHY.

ACETIC ACID.

Formula, $C_2H_4O_2$: Combining weight, 60.

Vinegar—which is weak acetic acid—was the only acid known to ancients. When alcoholic liquors—as wine or beer—are oxidized by fermentation, acetic acid is produced. Immense quantities of "wine vinegar" are made in France from the poorer classes of grape-juice, while "malt-vinegar" is now largely made in England. The oxidation of the alcohol is effected by a minute organism—the "vinegar-plant"—which exists in countless myriads in the liquid, and which absorbs oxygen from the air and then transfers it to the alcohol.

Strong acetic acid is obtained by adding sodium carbonate to vinegar, and then distilling the sodium acetate so formed with sulphuric acid.

When wood is heated in a retort an impure kind of acetic acid distills over. This is known as *pyroligneous acid* ; it is largely employed in commerce, and pure acetic acid can be readily prepared from it.

Pure acetic acid is a colorless liquid which solidifies at 62 deg. F., and forms large transparent crystals. Hence it is known as *glacial* (or ice-like) *acetic acid.* "Beaufoy's" acetic acid is a weaker form of the same substance, containing only thirty per cent. of the true acid.

Acetic acid mixes readily with water ; it has a strongly acid reaction, and a pungent smell and taste. It is very corrosive, blistering the skin. Acetic acid is a good solvent for many substances, including camphor and resins. As impurities abound in vinegar, that substance is not fit for use in ordinary chemical operations. But even the so-called pure acid frequently contains traces of sulphurous and hydrochloric acids, which may be detected by adding a little of the glacial acid to a solution of nitrate of silver. The mixture should remain colorless after it has been allowed to stand for several hours. Acetic acid often contains free sulphuric acid as an impurity. This may be detected by mixing with the acetic acid a little powdered starch. Boil, cool and add potassium iodide. A blue coloration indicates that free sulphuric acid is *absent*. But a blue coloration shows the *presence* of this acid, the starch being converted into glucose.

Acetic acid is used in the developer for collodion plates; also in printing upon bromide paper to prevent discoloration.

ALBUMEN.

Albumen is a very complex substance which exists in many modifications in both animals and plants. The albumen contained in white of egg (about 12 per cent.) may be taken as a typical example, and its formula may be written $C_{72}H_{112}O_{18}N_{22}SP$; but this can only be taken as giving a general idea of the chemical composition of this complex substance. The presence of sulphur in egg-albumen is proved by the well known blackening which silver egg-spoons undergo, and which is due to the formation of silver sulphide.

Egg-albumen also contains traces of sodium, chlorine and calcium phosphate, and the whole has a cellular structure. By beating up the white, the cells are broken, and the mineral impurities can then be removed by the addition, first, of basic lead acetate, and then of carbonic acid gas.

When egg-albumen is spread out in a thin layer and put in a warm place, it dries up to a yellow gum-like substance, which is the state in which it is usually sold by chemists.

This solid albumen is insoluble in alcohol or ether, but dissolves slowly in warm water, the solution being hastened by the addition of a little common salt. One part of solid albumen dissolved in seven parts of water yields a solution equal in strength to ordinary white of egg.

When liquid albumen is raised to a temperature of 150 deg. F., it begins to coagulate, and if the liquid be strong it is converted into a solid whitish mass; if dilute, it is simply rendered turbid. This coagulated albumen is insoluble in water.

Albumen is precipitated from its solutions by alcohol, by nitrate of silver, and by hydrochloric acid. Albumen is also present in blood, as *serum-albumen.* It is a good example of a *colloid* body; never crystallizing under any conditions. It may be separated from crystalloids by dialysis. The sulphur contained in albumen is one of the possible causes of the almost universal fading of prints on albumenized paper.

Albumen is largely used in photography, being universally employed to give a brilliant surface to the paper upon which photographic prints are produced (it was first used for this purpose by Fox Talbot, about 1852). Albumen was the first substance used to form a film in which the sensitive salts of silver could be spread out upon a glass plate, the albumen process being invented by Niepce de St. Victor, in 1847. This process is still employed for ordinary transparencies.

ALCOHOL (ETHYLIC ALCOHOL).

Formula, C_2H_6O: Combining weight, 46.

The term alcohol—spirits of wine—was originally applied only to the volatile inflammable liquid which is produced by the fermentation of sugar. The term has been extended, however, by chemists to numerous other bodies whose properties more or less resemble those of the liquid from which the class takes its name.

Ethylic alcohol, or spirits of wine, may be prepared either from the sweet juices of such fruits as the grape, or from a solution of cane-sugar, or from various kinds of grain, and the potato. By *fermentation*—due to the action of a minute plant—the sugary liquids are converted into alcohol and carbonic acid gas. The latter escapes, while the alcohol, mixed with water, remains.

To separate the spirit from the water, *distillation* is resorted to, the liquids being heated in a still. Now, the boiling-point of alcohol is only 173 deg. F. (that of water being 212 deg. F.), so that the more volatile alcohol passes away through the tube or worm of the still, leaving the water behind. But a certain quantity of water (about 10 per cent.) passes over with it, so that it is not possible to obtain pure or *absolute* alcohol by this method alone. The "rectified spirit" obtained by distillation repeated two or three times, usually has a specific gravity of .820 to .830 The next step is to add to the rectified spirit some substance, such as quick-lime or anhydrous copper sulphate, which will combine with and absorb the last traces of water. After distillation with this substance the absolute alcohol of commerce is obtained; but even this contains one-half per cent. of water. If, for experiment, it is necessary that even this small fraction should be removed, it may be done by adding a little metallic sodium and again distilling.

Absolute alcohol is a colorless, mobile liquid, has a pleasant smell, burning taste, and highly intoxicating properties. It burns readily with a bluish flame, and its vapor forms an explosive mixture with air. At freezing point (32 deg. F.) the specific gravity of alcohol is .806, and at 59 deg. F. it is .793. It quickly absorbs moisture from the air, so that it must be kept in glass bottles with carefully ground glass stoppers. To determine the amount of alcohol in any aqueous solution, an instrument called the *hydrometer* is generally employed. This consists of a closed glass or metal tube, upon which a scale is marked, and which is made to float upright by means of a loaded bulb at one end. As alcohol is less buoyant than water this instrument sinks deeper and deeper as the percentage of alcohol in the mixture increases, and by noting the point on the scale which is level with the surface of the fluid, the percentage of alcohol present can be determined by reference to printed tables constructed for the purpose.

TABLES SHOWING THE AMOUNT OF ALCOHOL, BY WEIGHT, PRESENT IN ANY MIXTURE OF ALCOHOL AND WATER.

TEMPERATURE, 60° F.

Specific gravity.	Alcohol by Weight	Specific gravity.	Alcohol by Weight.	Specific gravity.	Alcohol by Weight
.793	100	.882	66	.954	32
.798	99	.884	65	.956	31
.800	98	.886	64	.958	30
.803	97	.889	63	.959	29
806	96	.891	62	.961	28
.809	95	.893	61	.962	27
.812	94	.896	60	.964	26
.814	93	.898	59	.965	25
.817	92	.900	58	.966	24
.820	91	.903	57	.968	23
.823	90	.905	56	.969	22
.825	89	.907	55	.970	21
.828	88	.909	54	.971	20
.831	87	.912	53	.973	19
.833	86	.914	52	.974	18
.836	85	.916	51	.975	17
.838	84	.918	50	.976	16
.841	83	.920	49	.977	15
.843	82	.923	48	.979	14
.846	81	.925	47	.980	13
.848	80	.957	46	.681	12
.851	79	929	45	.983	11
.853	78	.931	44	.984	10
.856	77	.933	43	.985	9
.858	76	.935	42	.987	8
.860	75	.937	41	.988	7
.863	74	.939	40	.990	6
.865	73	.941	39	.991	5
.868	72	.943	38	.993	4
.870	71	.945	37	.994	3
.872	70	.947	36	.996	2
.875	69	.949	35	.998	1
.377	68	.951	34	1.000	0
.879	67	.953	33		

The high price of pure ethylic alcohol renders it an expensive liquid to use in any quantity. To meet the wants of manufacturers and men of science, a mixture (known as "methylated spirit") of ordinary alcohol with 10 per cent. of methyl alcohol is allowed to pass free of duty. It cannot, however, be sold without a license. Methyl alcohol is also known as wood-spirit, because it is obtained, along with acetic acid, from the dry distillation of wood. This admixture produces a nauseous taste, but for most purposes it answers as well as the pure alcohol.

Besides this "methylated spirit," or methylated alcohol," another liquid, known as "methylated finish," is sold, which contains a small quantity of resin. This renders it quite unfit for use in photography.

The photographic uses of alcohol are either as a solvent or a drier. Owing to the affinity of alcohol for water, it soon extracts that liquid from emulsions, wet gelatine plates, or soaked carbon tissue. Alcohol is also an ingredient of several developers. Fusel oil, a substance which is mostly amyl alcohol, is frequently present in ethylic alcohol as an impurity. It may be detected by the unpleasant odor remaining when a few drops of the liquid are rubbed between the hands, and by the faint red tint which it imparts to a solution of nitrate of silver in the suspected liquid when exposed to sunshine.

ALDEHYDE (ACETYL OR ACETIC ALDEHYDE).

Formula, C_2H_4O: Combining weight, 44.

The term aldehyde is applied to a series of compounds which are derived from the alcohol series by the elimination of some of their hydrogen. Acet-aldehyde is the one with which photographers are principally concerned. It is a colorless volatile liquid having an odor like sweet spirits of nitre. It is formed by the oxidation of ordinary alcohol, which may be effected by the presence of atmospheric oxygen, or by nitric acid, etc. Aldehyde almost always appears in the nitrate of silver bath used in the wet collodion process. It may be removed by pouring the bath into an open dish and exposing it to sunlight for a few hours. This "sunning the bath," as it was called, had frequently to be resorted to in the old "wet-plate" days; boiling has the same effect, but is not so safe a remedy. Acetic acid is also liable to contain traces of aldehyde.

The presence of aldehyde in photographic solutions is injurious, as it is a powerful reducing or deoxidizing agent and causes metallic silver to be deposited as a bright mirror. In this way, however, it improves the tone of collodion transparencies by completing the reduction of the silver forming the image. When aldehyde is oxidized it forms acetic acid ($C_2H_4O_2$).

CHAPTER XI.

CHEMICALS EMPLOYED IN PHOTOGRAPHY (CONTINUED).

ALUMINUM, OR ALUMINIUM.

Symbol, Al: Atomic weight, 27.

This metal (first isolated by Wöhler in 1828) is prepared by heating the mineral known as *cryolite* with sodium; also by the decomposition of compounds containing it in an electric furnace. Recent improvements in the manufacture have reduced the price of the metal from six dollars a pound to less than one dollar. Aluminum is a white, lustrous and very light metal; being little more than one-quarter the weight of copper—bulk for bulk. It does not rust in air. Owing to its lightness, aluminum is coming largely into use for lens-mounts, and for the metal parts of cameras, tripod-heads, etc.

ALUMINIUM AMMONIUM SULPHATE (AMMONIA ALUM).

Formula $Al_2 (SO_4)_3, (NH_4)_2 SO_4 + 24H_2O$.

When the ammonia liquor obtained in the manufacture of coal-gas is added to roasted coal-measure shale (which has been previously heated with sulphuric acid) ammonia alum is formed, which is then purified by crystallization. The appearance and properties of this salt are almost precisely similar to those of potash alum. Since the introduction of cheap potash salts from Stassfurt, in Germany, the manufacture of ammonia alum has almost ceased, potash alum taking its place.

ALUMINIUM POTASSIUM SULPHATE (COMMON POTASH ALUM).

Formula, $Al_2(SO_4)_3, K_2SO_4 + 24H_2O$: Combining weight, $516 + 252 = 768$.

Common potash alum is a double salt formed by the combination of the sulphates of aluminium and potassium. It is largely prepared by adding the latter compound to the roasted alum shales of the upper coal measures, which contain the former.

Potash alum forms transparent regular octahedral crystals (double pyramids), which are soluble in ten parts of cold, or one-third their weight of boiling water ; insoluble in alcohol. The solution has an acid reaction and an astringent taste. By exposure to air the crystals turn white, owing to the absorption of ammonia and the formation of a basic sulphate.

When heated they melt at 200 deg. F., in their water of crystallization, which then evaporates, leaving a white porous mass called burnt alum, which dissolves slowly in water.

In photography alum is mainly employed to give firmness and insolubility to gelatine films when soaked in it. In combination with citric acid it also clears films which have been discolored by the pyro developer. When "alum" is spoken of, the common potash alum is always to be understood.

Aluminium Nitrate.

Formula, $Al_2(NO_3)_6+16\ H_2O$: Combining weight, 326.

Prepared by dissolving aluminium hydrate in nitric acid, and evaporating the solution. It forms deliquescent needle-like crystals which are decomposed at a temperature of 302 deg. F., leaving a residue of alumina.

Aluminium nitrate is used as a mordant in calico printing.

Aluminium Sulphate.

Formula, $Al_2(SO_4))_3+18H_2O$: Combining weight, $342+324=666$.

Sulphate of alumina is produced commercially by decomposing china clay with sulphuric acid. It forms thin flat pearly plates, which dissolve in twice their weight of cold water. The pure salt for chemical purposes is prepared by adding aluminium hydrate to sulphuric acid.

Amber.

Amber is a fossil gum or resin which is found in the sandy coast of North Germany, fringing the Baltic Sea. It is hard, brittle, yellow, and more or less transparent. In photography it is used (by dissolving the powdered amber in chloroform or benzole) to make a varnish which can be applied cold to the surface of negatives.

AMMONIA.

Formula, NH_3 : Combining weight, 17.

True ammonia is a light, colorless gas, which has a pungent odor, and is so soluble in water that a pint of water at the ordinary temperature will dissolve 730 pints of gaseous ammonia. It is this solution—ammonium hydrate, NH_4HO—which is commonly called "ammonia," it is the "*liquor ammoniæ fort*" of druggists, and should have a specific gravity of .880. *Ordinary* "liquid ammonia," such as is used for pharmaceutical purposes, contains only ten per cent. of gaseous ammonia, and has a specific gravity of .936. By heat, the ammonia gas can be driven out of the water, and even under ordinary circumstances the gas escapes so rapidly that the solution is perceptibly weakened by simply pouring it from one bottle to another. For this reason it is best to dilute the strong liquor ammoniæ, immediately after it is purchased, with an equal bulk of water, and to keep it in a well-stoppered bottle; a corked bottle should never be employed for this liquid.

Ammonia gas is usually prepared by heating in a glass flask a mixture of quicklime and ammonium chloride. The ammonia gas which comes off will not burn unless it is first heated. The gas turns moist red litmus to an intense blue, and makes yellow turmeric paper brown. For this reason, and from its propensity to escape from solution, ammonia is known as the "volatile alkali." Carbonate and chloride of ammonia are not unfrequently present, as impurities, in commercial ammonia.

A trace of ammonia is always present in the air, and as some must be brought down by every shower, we see one way in which this substance—the essence of most manures—is naturally supplied to plants. Ammonia joins with the various acids to form ammoniacal salts, which greatly resemble the corresponding compounds of potassium and sodium. Any ammoniacal salt can be easily recognized by the evolution of ammonia, which occurs when the salt is warmed with a little slaked lime. All animal substances give off ammonia when they decay, or when they are heated. Formerly ammonia was mainly obtained by distilling the horns of deer in closed vessels, and hence its common name "spirits of hartshorn," or simply "hartshorn." The whole of the ammonia and ammonia salts of commerce are now derived from the "ammonia liquor" of gas-works. This liquor is neutralized with sulphuric or hydrochloric acid, and the resulting salts purified by crystallization, or by sublimation. Or a current of steam is blown through the liquor. This carries with it the ammonia, and is passed through dilute sulphuric acid, when crystals of ammonia sulphate separate out.

In photography ammonia is largely used to render the pyrogallic acid developer alkaline, the energy of its action being thereby greatly increased.

AMMONIUM.

Symbol, NH_4: Combining weight, 18.

Ammonium is one of those substances to which the name of *compound radicle* has been applied. It consists of the *two* elements, nitrogen and hydrogen; yet it can be transferred from one compound to another just as if it were an element It has never been obtained by itself; but its compounds behave in a similar manner to those of potassium. For these reasons chemists consider the group NH_4 as a quasi-metal, and the name *ammonium* has been applied to it.

AMMONIUM BICHROMATE.

Formula, $(NH_4)_2Cr_2O_7$: Combining weight, 252.

Prepared by adding chromium trioxide to ammonia. Another method is to divide a solution of chromic acid into two parts; neutralize one part with ammonia, then add the other part and evaporate. Ammonium bichromate is a crystalline substance, soluble in water. When a little of the solution is added to a solution of albumen, or gelatine, and exposed to light it renders these substances insoluble in those liquids which would otherwise dissolve them. The cause of this appears to be that the bichromate suffers reduction by the action of the light, parting with some of its oxygen, which goes to the albumen, etc. The oxidized albumen, or gelatine, is insoluble in warm water and other solvents which readily dissolve the normal substance. Used in this manner the bichromate of ammonia renders great service in certain photographic processes.

AMMONIUM BROMIDE.

Formula, NH_4Br: Combining weight, 98.

May be prepared by adding potassium bromide to a solution of ammonia, and evaporating, or by passing ammonia into hydrobromic acid. Its crystals are cubical and colorless; very soluble in water, less soluble in alcohol and ether. This salt keeps well, but in contact with moist air it turns yellow, owing to the separation of bromine. When strongly heated it sublimes without fusing.

Ammonium bromide is largely used in photography. As an ingredient of the ordinary pyro developer it exercises a restraining action on the silver salts present in the film, thereby tending to the prevention of fog.

AMMONIUM CARBONATE.

Formula, $(NH_4)_2CO_3$: Combining weight, 99.

Carbonate of ammonia (often called "smelting salts," and "sal volatile") is made by heating a mixture of ammonium chloride and chalk. It is usually sold as a fibrous translucent solid, which smells distinctly of ammonia. It is insoluble in alcohol; but soluble in three times its own weight of water. Ammonium carbonate may be used as the alkali in the pyro developer. It gives a pink tone to lantern slides and transparencies.

AMMONIUM CHLORIDE.

Formula, NH_4Cl: Combining weight $53\frac{1}{2}$.

Prepared by adding hydrochloric acid to the ammoniacal liquor obtained from coal in the manufacture of coal-gas. It is purified by heating until it sublimes, which it does without previous fusion. When prepared in this way on a large scale it forms tough, fibrous whitish lumps, which are soluble in three parts of cold or one part of boiling water; insoluble in absolute alcohol.

Ammonium chloride is largely used for "salting" paper which is to be subsequently sensitized with the silver nitrate bath.

Ammonium Citrate.

Formula, $C_6H_5(NA_4)_3O_7 + 3H_2O$: Combining weight, $243 + 54 = 297$.

Prepared by neutralizing a solution of citric acid with ammonia. It is a powerful restrainer, and is of great service in the development of over-exposed negatives. As soon as all detail is out, the negative should be transferred to a three-per-cent solution of the citrate. After soaking for five minutes, development may be resumed; when the negative will be found to intensify, without fog appearing.

Ammonium Iodide.

Formula, NH_4I: Combining weight, 145.

Prepared by adding ammonium sulphate to a hot saturated solution of potassium iodide. Alcohol is then added to precipitate the potassium sulphate formed, which is then filtered off, and the remaining solution evaporated, by which colorless cubes of ammonium iodide are obtained.

This salt is a favorite in the collodion process, as it imparts to the collodion "limpidity, sensitiveness, and adherency to the glass." It is rather liable to decompose, especially when in contact with air, liberating iodine, which is known by its yellow color. This tendency may be checked by the admixture of cadmium iodide.

Ammonium Nitrate.

Formula, $(NH_4)\,NO_3$: Combining weight, 80.

This salt may be prepared by neutralizing solutions of ammonia or ammonium carbonate with nitric acid.

On evaporation it crystallizes out in hexagonal prisms, which dissolve (producing great cold in so doing) in their own weight of water.

Ammonium nitrate is decomposed by heat into nitrous oxide and water.

AMMONIUM SULPHYDRATE.

Formula, $(NH_4)HS$: Combining weight, 51.

Prepared as an aqueous solution by passing sulphuretted hydrogen through an aqueous solution of ammonia. It can also be obtained in the crystalline form by passing the same gas through an alcoholic solution of ammonia. Ammonium sulphydrate turns yellow when exposed to the air for any length of time. It precipitates many metals as sulphides, and is often used in this way to recover silver from solutions containing it. It is also useful as an intensifier.

ANTIMONY SULPHIDE.

Formula, Sb_2S_3: Combining weight, 340.

Occurs native as a shining crystalline substance, having a leaden-gray color and a radiated structure. It may be prepared by heating together antimony and sulphur; or by passing a current of sulphuretted hydrogen through a solution of tartar emetic or any other soluble antimonious salt, when it appears as an orange-colored precipitate.

ARSENIC BROMIDE.

Formula, $AsBr_3$: Combining weight, 315.

Prepared by dissolving powdered arsenic in a solution of bromine in carbon bisulphide, and evaporating. It forms colorless deliquescent crystals, which melt at about 70 deg. F., and are decomposed by water.

ASPHALTUM.

Asphaltum, bitumen, or bitumen of Judea, is a term which includes several substances occurring naturally in the earth. They are of a brownish-black color, with a peculiar "bituminous" smell, and occur chiefly in volcanic regions, such as the Dead Sea, in Syria, the great Pitch Lake on the island of Trinidad, Cuba, Peru, etc. Chemically they are sulphuretted hydro-carbons, and were probably formed by the action of heated sulphur upon petroleum, or some similar body, underground. Analysis gives the average percentage composition as carbon 80, hydrogen 10, sulphur 9, nitrogen and ash 1.

The term bitumen is usually employed for the softer or more fluid kinds, while the name asphaltum, or asphalt, is applied to the hard varieties. Asphaltum is partially soluble in alcohol, ether or benzole; very soluble in chloroform, carbon bisulphide, and turpentine. Asphalt is the foundation of most of the black varnishes now in use. In photography this substance has a special interest, as it was upon metal plates covered with a thin layer of asphalt that Niepce obtained the first permanent photographs about the year 1824.

Asphalt is affected by light with the result that it is rendered insoluble in its usual *menstrua*. For this reason it has long been employed in photo-lithography, in which its indifference to acids is also of value. Nicephore Niepce first employed asphalt in this way, in 1824, in his photographic process called *heliography*.

AZALINE.

This is the commercial name for a mixture made by dissolving 30 grains of quinoline-red and 3 grains of quinoline-blue or cyanin in 40 ounces of alcohol. It is used to produce isochromatic effects; causing plates which are bathed in the solution to become more sensitive to the yellow and red rays.

BARIUM.

Symbol, Ba.: Combining weight, 137.

Metallic barium was not obtained until the year 1808, when Davy isolated it by the electrolysis of baric chloride. It is a yellow metal, as easily oxidized as sodium, decomposing water at the ordinary temperature.

BARIUM CHLORIDE.

Formula, $BaCl_2+2H_2O$: Combining weight, $208+36=244$.

Prepared by dissolving barium carbonate in hydrochloric acid. The colorless crystals of barium chloride usually met with are fairly soluble in water, and the solution is used as a test for sulphuric acid or any soluble sulphate. The presence of these substances is indicated by a heavy white precipitate of barium sulphate, insoluble in all acids except hot, strong sulphuric acid.

Barium Hydrate.

Formula, $BaH_2O_2+8H_2O$: Combining weight, $171+144=315$.

Made by dissolving barium nitrate in a hot solution of caustic soda. It forms white crystals which are soluble in twenty times their weight of water; insoluble in alcohol. Also known as "baryta," and as "barium hydroxide."

The solution absorbs carbonic acid from the air and soon becomes milky. Dr. A. H. Elliott states that barium hydrate acts as an accelerator with hydroquinone; no bromide must be used.

Barium Nitrate.

Formula, $Ba(NO_3)_2$: Combining weight, 261.

Barium nitrate is commonly called "nitrate of baryta." It is prepared by dissolving barium carbonate or sulphide in dilute nitric acid. Its crystals are soluble in twelve parts of cold, or three of boiling, water; insoluble in nitric acid or in alcohol.

The addition of a little barium nitrate to the silver nitrate bath used in the wet collodion process prevents the formation of "pin-holes."

Benzole (or Benzene).

Formula, C_6H_6: Combining weight, 78.

Commercially, benzole is obtained from coal-tar oil, of which it is the most volatile constituent. It is a white solid which melts at 42 deg. F. to a clear, limpid liquid having a peculiar and rather pleasant smell; it boils at 177 deg. F., and the vapor burns with a bright but smoky flame. Benzole is not soluble in water but dissolves freely in alcohol, ether, and oil of turpentine. It is an excellent solvent for caoutchouc and gutta-percha, and dissolves fats and oils with such facility that it is in general use for removing grease spots.

BROMINE.

Symbol, Br: Combining weight, 80.

The element bromine was first obtained by Balard, in 1826, from the salts left by the evaporation of sea-water. It is a dark-red, heavy liquid, which becomes a black solid when its temperature is lowered to eight degrees below zero (F.), and which boils at 145 deg. F. There are only two elements which are liquid at ordinary temperatures; bromine is one and mercury the other. Bromine has a strong irritating smell, and is very poisonous. It is prepared by heating potassium bromide with sulphuric acid and black oxide of manganese.

$$\underset{\text{Potassium bromide.}}{2KBr} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Manganic oxide.}}{MnO_2} = \underset{\text{Bromine.}}{Br_2} + \underset{\text{Potassium sulphate.}}{K_2SO_4}$$

$$+ \underset{\text{Manganese sulphate.}}{MnSO_4} + \underset{\text{Water.}}{2H_2O}$$

CHAPTER XII.

CHEMICALS EMPLOYED IN PHOTOGRAPHY (CONTINUED).

CADMIUM.

Symbol, Cd: Combining weight, 112.

This metal was discovered in 1817. It is usually found combined with zinc in the various ores of the latter metal, and for this reason zinc is a common impurity in the commercial salts of cadmium. Cadmium is a white lustrous metal, resembling tin. It is attacked by the stronger acids. Zinc precipitates metallic cadmium from any solution containing it. In photography powdered cadmium is sometimes used to remove free iodine from collodion.

CADMIUM BROMIDE.

Formula, $CdBr_2 + 4H_2O$: Combining weight, $272 + 72 = 344$.

Prepared by digesting powdered metallic cadmium with bromine and water. By evaporating the solution, needle-shaped crystals of $CdBr_2$, combined with four equivalents of water, are obtained. By heating carefully in a porcelain crucible the water of crystallization may be removed.

Owing to the stability of this salt, and its solubility in collodion, alcohol, and ether, it has been much used as a source of the bromine which is required for the production of silver bromide—the sensitive compound now so universally employed in photography.

CADMIUM IODIDE.

Formula, CdI_2: Combining weight, 366.

Prepared by digesting the powdered metal with iodine and water. By evaporating the solution cadmium iodide is obtained in flat, pearly crystals. It is soluble in water, and is also one of the few iodides which are soluble in alcohol. For the latter reason it is largely used in photography for the purpose of iodizing the collodion used in the wet process.

Calcium Bromide.

Formula, $CaBr_2$: Combining weight, 200.

Obtained in silky needles when hydrobromic acid is passed into an aqueous solution of calcium hydrate (slaked lime), and the liquid evaporated. Its properties are similar to those of calcium chloride.

Calcium Carbonate.

Formula, $CaCO_3$. Combining weight, 100.

Carbonate of lime occurs plentifully as limestone, chalk, marble, and Iceland spar; the last two forms being nearly pure. Insoluble in alcohol, and in pure water; slightly soluble in water which contains carbonic acid gas. "Whiting," or "whitening," is powdered chalk; it is used to neutralize acidity in the ordinary gold toning baths.

Calcium Chloride.

Formula, $CaCl_2 + 6H_2O$: Combining weight, $111 + 108 = 219$.

Prepared by dissolving marble (calcium carbonate) in hydrochloric acid; also obtained as a bye-product in the manufacture of ammonia and potassium chlorate.

Calcium chloride forms large transparent crystals, which are extremely soluble in water, producing great cold, and deliquesce when exposed to the air. It is also freely soluble in water. By a strong heat the water of crystallization can be driven off, and the pure anhydrous salt remains as a white or colorless mass. In this state it greedily absorbs water, and is much used for drying gases and liquids. For the latter purpose it is best to place lumps of the anhydrous fused salt in the liquid. Of course, only liquids in which calcium chloride is not soluble can be dried in this way. Gases are usually dried by passing them through tubes full of small lumps of the white salt. The air in the box used for drying gelatine plates can be dried by keeping a metal box filled with calcium chloride at the bottom of the box. Calcium chloride (wrapped in tissue-paper and cotton-wool) is also used to dry the air in the paper or metal tubes in which platinotype paper is usually kept.

CALCIUM HYDRATE.

Formula, CaH_2O_2 : Combining weight, 74.

Made by pouring water upon quicklime. Is also known as "slaked lime," and as "calcium hydroxide." Soluble in 700 times its own weight of water, the solution being known as "lime-water." Is sometimes used in photography in the gold toning bath. In the hydroquinone developer lime-water (combined with sulphite of soda and sugar) acts as an energetic accelerator.

CALCIUM IODIDE.

Formula, CaI_2 : Combining weight, 294.

Prepared by dissolving calcium carbonate in hydriodic acid. In its properties it resembles calcium chloride. When heated in air it parts with the whole of its iodine, and forms calcium oxide.

CALCIUM OXIDE (QUICKLIME).

Formula, CaO : Combining weight, 56.

Ordinary "quicklime" is prepared by heating carbonate of lime (limestone) in kilns, the heat driving off the carbonic acid gas:

$$\underset{\text{Carbonate of lime.}}{CaCO_3} = \underset{\text{Quicklime.}}{CaO} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Quicklime rapidly absorbs moisture from the air, and crumbles away; hence it should be kept in well-stoppered bottles. Cylinders of hard quicklime heated by an oxy-hydrogen flame are used as a source of light in the oxy-hydrogen lantern.

CAMPHOR.

Formula, $C_{10}H_{16}O$: Combining weight, 152.

Camphor is obtained by steaming the wood of the *camphor laurel*, a tree which grows in China and Japan. It is a white or colorless crystalline solid of penetrating odor, only slightly soluble in water, but soluble in alcohol and ether. Camphor is also soluble in turpentine, and the solution, mixed with a little emery, is very useful in grinding glass stoppers into the necks of bottles so as to secure a perfect fit, or for grinding glass for any purpose. Camphor is very tough, but can readily be pounded up when mixed with a little of any of the liquids which dissolve it. It is used as a preservative, keeping off the attacks of insects and bacteria, and so preventing solutions of gelatine, albumen, etc., from becoming mouldy.

The addition of a little camphor (a piece about the size of a nut to each pint) to the oil used in magic lanterns is found to increase the brilliancy and whiteness of the light.

CANADA BALSAM.

Canada balsam is a resinous substance containing much essential oil, which causes it to be soft and viscous. It exudes from incisions made in the stem of a species of pine-tree (*Pinus balsamæ*), which grows abundantly in Canada. From its liquid and colorless sticky nature it is much used by opticians for cementing together the components of achromatic lenses. Some samples, after long exposure to light, turn yellow, while others crack and show the "colors of thin plates," causing a fear that the lens is damaged. When this is the case the lens should be removed from its brass mount and soaked in warm turpentine, which will dissolve the cement. The ordinary Canada balsam of commerce is of a yellowish hue, but it can be decolorized by exposing the yellow balsam in clear white glass bottles to sunlight.

Canada balsam dissolved in benzole renders paper translucent.

CAOUTCHOUC.

Caoutchouc, more familiarly known as India-rubber, is the solidified juice which exudes from certain tropical plants.

When protected from air and light (as by being kept in water in a dark place) it undergoes no change, but under ordinary conditions it absorbs oxygen from the air, and becomes rotten and inelastic in the course of a few months.

Freshly cut edges of caoutchouc adhere firmly when brought into contact, and it is invaluable in the laboratory for the construction of tubing, etc. Washed ether, chloroform, carbon bisulphide, coal-naphtha, and rectified oil of turpentine are all able to dissolve caoutchouc. It is insoluble in alcohol. When caoutchouc is heated with 2 or 3 per cent. of sulphur, the compound known as vulcanized India-rubber is formed. If the percentage of sulphur be increased to 12 or 15, the heated mixture becomes hard, black, and horny, and is known as ebonite or vulcanite.

Gutta-percha is the hardened juice of a tree which grows in Singapore, Borneo, etc. Its properties are similar to those of caoutchouc.

Carbolic Acid (Phenol).

Formula, C_6H_6O: Combining weight, 94.

Coal-tar is the principal source of carbolic acid. When purified it crystallizes in colorless needles, which melt at 102 deg. F. It is soluble in water, and still more soluble in alcohol, ether, and acetic acid. Although called an acid, it does not redden litmus paper. Of late years carbolic acid has been largely used as a disinfectant, and as a preventer of putrefaction and fermentation. These valuable qualities appear to be due to its power of coagulating albumen. When a few drops of an aqueous solution of carbolic acid are added to albumen, gum, etc., decay or mould will be prevented. Carbolic soap contains from five to twenty per cent. of the acid, and is most useful, not only for general purposes, but in special cases where a disinfectant is required.

Carbon.

Symbol, C: Combining weight, 12.

Carbon is found free in nature as the mineral graphite (commonly called black-lead or plumbago), and crystallized as the diamond. Coal usually contains from three-quarters to nine-tenths its weight of carbon. All organic compounds contain carbon, and they give evidence of this by *blackening* when heated. In this way we often notice the presence of this element in bread, meat, etc.

By heating coal, wood, or bones in iron retorts, the gases these substances contain are driven off, and the forms of carbon known as coke, charcoal, and bone black are left behind. Lamp-black is a finely divided form of carbon deposited from burning oil or tallow; and in the same way we get gas-black by holding some cold incombustible body in a gas flame.

Carbon has never been melted or dissolved. Amorphous carbon or charcoal has a remarkable power of absorbing and condensing gases. In this way it destroys bad smells, and prevents putrefaction. It also retains the coloring matter of liquids passed through it, and is used for this purpose in the purification of raw sugar, and in filters, etc.

Carbonic Acid Gas.

Formula, CO_2 : Combining weight, 44.

Carbonic acid gas is chemically known as *carbonic anhydride*, because, when added to water, it produces a feeble acid —the true carbonic acid, H_2CO_3. But this acid cannot be obtained pure, and its aqueous solution is very unstable. Carbonic acid gas is usually prepared by the action of dilute hydrochloric acid on marble (calcium carbonate); but it is released whenever one of the carbonates is treated with a stronger acid, and is formed whenever carbon, or any substance containing carbon, is burnt in the air.

Carbonic acid gas is colorless; it will not burn, nor will it support combustion; it is so heavy that it can readily be poured, like a liquid, from one vessel to another. Animals soon die when placed in an atmosphere of this gas, and many human lives have been lost owing to its accumulation at the bottom of old wells, brewers' vats, etc. By cold and pressure combined, carbonic acid gas can be reduced to a colorless liquid whose evaporation can be made to produce a most intense cold—.166 deg. F.

Commercially, carbonic acid gas is largely used in the manufacture of effervescent drinks, such as soda-water, ginger-beer, etc., the gas being forced into the liquid by pressure.

The sparkling appearance of spring-water, champagne, and most aerated waters is due to the presence of carbonic acid gas.

Castor Oil.

This is a viscid oil obtained from the seeds of the "castor oil plant," *Ricinus communis.* It slowly hardens by long exposure to the air, but does not solidify even at 0 deg. F. It is soluble in alcohol. When a small quantity of castor oil is mixed with collodion it toughens the film so that it can be more readily transferred from the glass plate to some other support. It also imparts a toughness to varnishes.

Chlorine.

Symbol, Cl; Combining weight, 35½.

Chlorine was discovered by Scheele, in 1774. It is never found free in nature, but occurs plentifully combined with sodium (as common salt, $NaCl$), and with many other metals, forming binary compounds called chlorides.

It is a greenish-yellow heavy gas, possessing a powerful and disagreeable smell (something like that of sea-weed). It is very dangerous to inhale chlorine; hence it should always be prepared in the open air or where there is a free draught.

For this purpose we may mix one ounce of salt with one ounce of black oxide of manganese in a glass retort, and then add two ounces of sulphuric acid, previously diluted with an equal quantity of water. When a very gentle heat is applied, chlorine gas will come off in abundance. It should be washed by passing it through water.

By submitting chlorine to a pressure of about seventy-five pounds per square inch, it is converted into a heavy yellow liquid.

Chlorine is very soluble in water, and the solution—known as "chlorine-water"—is used for many purposes instead of the pure gas. Its powers of combination with other elements are very marked. A mixture of chlorine with hydrogen explodes when exposed to sunlight or to the light of burning magnesium, the two elements combining to form hydrochloric acid gas.

When metals in the state of a fine powder are dropped into chlorine gas, they take fire spontaneously, and the chlorides of the metals are formed.

Chlorine bleaches all animal and vegetable colors, and it is largely used for this purpose in the manufacture of paper, of cotton, and of linen. If all traces of chlorine are not removed after bleaching is effected, the substance will rapidly rot. Hyposulphite of soda—the photographer's bane—is frequently used to effect this complete removal of the last traces of chlorine, and is hence termed an "anti-chlor."

CHLORINETTED LIME (CALCIUM CHLORO-HYPOCHLORITE OR BLEACHING POWDER).

Formula, $Ca(OCl)Cl$: Combining weight, 127.

This substance is commonly known as "chloride of lime" and as "bleaching powder." Chemists are not fully agreed respecting its chemical nature, some regarding it as a *mixture* of calcium chloride with calcium hypochlorite, while others consider it to be a true chemical compound—calcium chloro-hypochlorite.

Bleaching powder is made on a very large scale in the alkali works of South Lancashire. The floors of large chambers are covered with dry slaked lime, and the chambers are then filled with chlorine gas, which combines with the lime. Commercial bleaching powder contains from twenty-five to thirty-five per cent. of available chlorine. It is a white powder, which has a faint smell of hypochlorous acid, and attracts moisture from the air. For bleaching purposes the articles are first dipped in a clear dilute solution of the bleaching powder, and then placed in very dilute hydrochloric acid. In this way chlorine is liberated, which combines with the coloring matters to form colorless compounds.

Under the name of "chloride of lime," bleaching powder is largely used as a disinfectant. In photography it is used as an ingredient of a toning bath which gives black tones.

CHLOROFORM.

Formula, $CHCl_3$: Combining weight, $119\frac{1}{2}$.

Chloroform can be prepared in several ways, as by distilling bleaching powder with very dilute alcohol, or by the action of chlorine on marsh gas. It is a colorless, heavy, volatile liquid, having a strong and rather agreeable smell. When inhaled it produces perfect, though temporary, insensibility to pain. It is a good solvent for sulphur, phosphorus, and iodine, and for most fatty and resinous bodies, especially caoutchouc. It has no action on collodion, and does not mix with water; it dissolves readily in alcohol.

CHLOROPHYLL.

The name given to the green coloring matter of plants. It is prepared by treating chopped leaves (young myrtle leaves answer well) with warm alcohol for ten minutes, and then filtering. It should be kept in an opaque bottle, with a little powdered zinc. Chlorophyll is insoluble in water; soluble in alcohol and in ether. It has been successfully used by Ives and others to render gelatine plates more sensitive to the red and yellow rays.

CHROMIUM POTASSIUM SULPHATE (CHROME ALUM).

Formula, $Cr_2(SO_4)_3, K_2SO_4+24H_2O$: Combining weight, $566+432=998$.

Prepared by passing sulphurous acid gas through a mixture of potassium bichromate and sulphuric acid. Also obtained as a bye-product in the manufacture of alizarine.

Chrome alum forms octahedral crystals, dark-red—almost black—in color, soluble in seven parts of water.

Chrome alum is employed in tanning. In photography it is used to toughen and render insoluble the films of gelatine used in the manufacture of dry-plates.

CITRIC ACID.

Formula, $C_6H_8O_7+H_2O$: Combining weight, $192+18=210$.

Citric acid is principally prepared from the juice of lemons, by the addition first of powdered chalk and then of sulphuric acid, the chalk forming calcium citrate, which is decomposed by the acid. Citric acid forms transparent crystals, which are very soluble in water and in alcohol. Being a tri-basic acid, it forms three series of citrates, of which those of the alkalies are soluble in water. When added to the pyro developer, citric acid checks strongly the reduction of the silver salt, so that it is frequently used as a retarder, being especially useful in hot weather, or when the exposure has been much too long.

COLLODION.

In 1847, Maynard, in America, discovered that a certain form of pyroxyline was soluble in a mixture of alcohol and ether, and that as these solvents evaporated the pyroxyline was left behind as a delicate transparent skin or film. To the substance so obtained the name of *collodion* was given, and it was found to be of service in surgery to form a covering to raw places on the skin to keep away the air.

In 1850, Scott Archer applied the new material to photographic purposes, using it to coat glass plates, and to receive and hold the sensitive salts which were to be affected by light. From 1850 to 1878 the "collodion process" was almost universally employed by photographers, but the advent of gelatine dry-plates in the latter year has since caused it to hold a secondary position.

For general work a good collodion may be made by taking half a pint of alcohol (sp. grav., .820) and the same quantity of ether (sp. grav., .725), and dissolving in the mixture 115 grains of pyroxyline. In cold weather half an ounce *less* alcohol and half an ounce *more* ether may be used with advantage.

Photographers almost always purchase collodion ready-made, since the great manufacturing firms who have made its preparation a specialty are able to produce a better article at a less cost than any individual could hope to do.

COPPER BROMIDES.

Copper combines with bromine in two proportions to form cuprous bromide (Cu_2Br_2) and cupric bromide ($CuBr_2$); the combining weights are 287 and 223, respectively.

Cuprous bromide is a brown crystalline substance, which becomes blue when exposed to sunlight. It can be prepared by heating copper filings in contact with bromine.

Cupric bromide is formed as dark-colored deliquescent crystals when cupric oxide is dissolved in hydrobromic acid and the solution evaporated *in vacuo.*

COPPER NITRATE.

Formula, $Cu(NO_3)_2+H_2O$: Combining weight, $187+54=241$.

Copper nitrate is produced by the action of nitric acid on metallic copper, or on cupric oxide. It forms blue prismatic crystals, which are very soluble in water and in alcohol. Copper nitrate readily parts with oxygen, and is used as an oxidizing agent in dyeing and in calico printing. It imparts a green color to the flame of a spirit-lamp or Bunsen burner.

COPPER SULPHATE.

Formula, $CuSO_4+5H_2O$: Combining weight, $159+90=249$.

Copper sulphate, cupric sulphate, or *blue vitriol*, is obtained in large blue crystals by dissolving copper oxide in dilute sulphuric acid and evaporating the solution. It often contains ferrous sulphate as an impurity.

CYANIN.

Formula, $C_{28}H_{35}N_2I$: Combining weight, 526.

Also known as chinolin blue, or quinolin. Sold as a coarse dark-green powder of metallic lustre, which is slightly soluble in water, more so in alcohol. Used to increase the sensitiveness of gelatine dry-plates to the red rays.

CYANOGEN.

Formula, $(CN)_2$, or Cy_2 : Combining weight, 52.

The important organic compound called cyanogen was discovered by Gay Lussac in 1814. Cyanogen gas can be obtained by strongly heating dry mercuric cyanide in a glass tube. It is transparent and colorless, and burns with a beautiful rose-edged, purple flame. Cyanogen is very soluble in water and in alcohol. Cyanogen is important as being the first known of the "compound radicals—compounds which can be transferred bodily from one chemical compound to another, just like elements. Its "compound atom" (CN) forms part of many organic substances. Cyanogen may be readily liquefied by heating mercuric cyanide in a bent tube, sealed at both ends.

DEXTRINE.

Also known as "British Gum." Made by moistening starch with dilute nitric acid, and then drying and heating. Sold as a brown powder which dissolves in hot water and is then used for mounting prints. Dextrine is the adhesive generally used to coat the backs of postage-stamps.

EIKONOGEN.

In 1881 Professor Raphael Meldola prepared a new substance, to which he gave the name of amido-beta-naphthol-sulphuric acid.* Its chemical formula is $C_{10}H_5NH_2,OH,SO_3H$, and Meldola obtained it by the reduction of nitroso-beta-naphthol-sulphuric acid. It was soon afterwards obtained more cheaply by other processes by Dr. Witt, in Germany; and is now manufactured by the Actiengesellschaft für Anilinfabrikation in Berlin.

Eikonogen is the sodium salt of this acid; and its chemical name is therefore sodium-amido-beta-naphthol-sulphonate. Its formula is $C_{10}H_5NH_2,ONa,SO_3H$. Eikonogen is sold in yellowish-white crystals which are moderately soluble in water; insoluble in alcohol. Like pyro, hydroquinone, etc., eikonogen is able to reduce silver salts, and it forms a valuable developing agent. It is not poisonous.

ERYTHROSINE.

Formula, $C_6H_4[COC_6HI_2(ONa)_2]_2$: Combining weight, 830.

This is a reddish-brown powder obtained by the action of

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*[*Journal of the Chemical Society*, vol. xxxix., p. 47.

iodine upon fluorescëin. It is also known as "eosin blue-shade," and as "erythrosin B." It is very soluble in water. Erythrosine is the substance commonly employed to render gelatine emulsion or dry-plates sensitive to yellow and green light; and plates so prepared are known as "isochromatic," "orthochromatic," or color-sensitive." Its use (in conjunction with ammonia) for this purpose was patented by Attout-Tailfer in 1882.

ETHER (SULPHURIC ETHER).

Formula, $C_4H_{10}O$: Combining weight, 74.

Ether is prepared on a large scale by distilling alcohol with sulphuric acid. It is a colorless, very mobile liquid which has a specific gravity of from .720 to .736, and a boiling point of 94 deg. F. Ether is a transparent and light liquid having a fragrant and exhilarating smell. It mixes readily with alcohol, but scarcely at all with water. It dissolves fats and resins; also bromine and iodine, and most metallic bromides and iodides.

The boiling point of ether is so low, and it vaporizes so readily, that it is dangerous to bring a light near to an unstoppered bottle containing it. Pure ether becomes acid by exposure to light, so that it should always be kept in a dark and cool place. This acid condition may be detected by the yellow color such ether produces when shaken up with an aqueous solution of iodide of potassium. Ether is sometimes adulterated with water, but the latter may be tested for by mixing a little of the ether with spirits of turpentine. If any water is present a turbidity is produced. Methyl, or wood spirit, is sometimes added, but this may be known by the smell, and its discharging in a few hours the color produced by adding one drop of tincture of iodine to an ounce of the ether. One of the best signs, however, of pure sulphuric ether is its low specific gravity.

ETHER, METHYLATED.

Just as pure ether is made by distilling a mixture of alcohol and sulphuric acid, so methylated ether is made by distilling methylated spirit with the same acid.

As methylated spirit is much cheaper than pure alcohol, so the methylated ether produced is cheaper than pure ether. Since it answers almost equally as well as pure ether in the manufacture of collodion, the methylated ether is now universally used by large preparers of that article. Its odor is, however, stronger and more disagreeable than that of pure ether, and the nitrate of silver bath is more easily disorganized by it.

Ether, Methylic.

Formula, C_2H_6O: Combining weight, 46.

Methyl ether, or methylic ether, is also known as methyl oxide. Although it is composed of the same elements, in the same proportions, as alcohol, yet its properties are very different, a fact which chemists explain by believing that the atoms which form its molecule are differently arranged. Methylic ether is prepared by distilling one part of methyl alcohol (or pyroxylic spirit, CH_4O), with four parts of oil of vitriol, and purifying the distillate with slaked lime.

It is a colorless gas, very soluble in water, and still more so in alcohol or ether. It burns with a pale flame.

Ferrous Oxalate.

Formula, FeC_2O_4: Combining weight, 142.

Oxalate of iron is a yellow powder, which is formed as a precipitate when a solution of oxalic acid (one ounce to 16 ounces of water) is added to an equal bulk of a solution of ferrous sulphate ($2\frac{1}{4}$ ounces to 16 ounces of water to which a few drops of sulphuric acid have been added). Allow to stand all night; then decant off the clear liquid and wash and dry the precipitate. Ferrous oxalate is insoluble in water, but readily dissolves in a solution of potassium oxalate, forming a rich red solution of potassium ferrous oxalate, $K_2Fe(C_2O_4)_2$. In this state it forms a clear and vigorous developer, which is especially used for bromide paper and for transparencies. This developer is generally made by adding a saturated solution of ferrous sulphate to a saturated solution of potassium oxalate (1 part of the former to 4 parts of the latter) but when produced in this way it must not be forgotten that sulphate of potassium is also formed, and this acts as a restrainer.

FLUORINE.

Symbol F: Combining weight, 19.

This element, the most chemically active of the four halogens, is most frequently met with in combination with the metal calcium, as beautiful cubical crystals of calcium fluoride, CaF_2 (commonly called fluor-spar).

Fluorine has a remarkable chemical affinity for all the other elements except oxygen. It was not obtained in the separate or free state till 1887, when M. Henri Moissan succeeded in obtaining it by passing a current of electricity through potassium fluoride dissolved in anhydrous hydrofluoric acid. Fluorine is a colorless gas, having a penetrating and disagreeable odor, and an irritating effect when inhaled. It combines instantly with almost all substances, even such refractory bodies as silicon, boron, etc., igniting spontaneously when brought into contact with it.

FORMIC ACID.

Formula, CH_2O_2: Combining weight, 46.

This acid occurs in the bodies of red ants, in the hairs of certain species of caterpillars, and in stinging nettles.

It is usually prepared by distilling a mixture of oxalic acid and glycerine.

Formic acid is a clear, colorless, inflammable, corrosive liquid, which acts as a powerful reducing agent. It has been strongly recommended as a preservative for solutions of pyrogallol.

When heated with silver nitrate, carbonic acid gas is evolved and metallic silver deposited; similarly mercuric chloride is reduced to mercurous chloride or calomel. This reducing action seems to distinguish formic acid from acetic acid and its homologues.

FREEZING MIXTURES.

By a mixture of certain chemicals, or other substances, it is possible to temporarily produce a degree of cold far below the freezing-point of water. It is advantageous to place the mixture in some thick vessel, well surrounded by flannel or some other non-conducting substance, to prevent the access of heat. The substance to be cooled should be placed in a thin vessel, which should be inserted in the middle of the freezing mixture. Thus the street vendors of "ice-cream" put the dainty in a tin, which stands in a freezing mixture contained in a bucket well wrapped up in flannel.

Some of the best-known freezing mixtures are given below, together with the degree of cold each is capable of producing.

FREEZING MIXTURES WITHOUT ICE.

Mixtures.	Thermometer falls.	Degree of cold produced.
Ammonium nitrate, 1 part............. Water, 1 part...........................	From 50 deg. to 4 deg.	46 deg
Ammonium chloride, 5 parts........... Potassium nitrate, 5 parts .... Water, 16 parts........................	From 50 deg. to 10 deg.	40 deg
Sodium sulphate (Glauber's salt), 3 parts. Dilute nitric acid, 2 parts.............	From 50 deg. to -3 deg.	53 deg
Sodium sulphate, 8 parts............... Hydrochloric acid, 5 parts..............	From 50 deg. to 0 deg.	50 deg
Sodium sulphate, 6 parts.............. Ammonium nitrate, 5 parts............. Dilute nitric acid, 4 parts...............	From 50 deg. to -14 deg.	64 deg

FREEZING MIXTURES WITH ICE.

Mixtures.	Thermometer falls.	Degree of cold produced.
Snow (or powdered ice), 2 parts. .... Common salt, 1 part.........................	From any temperature to 5 deg. below zero.	......
Snow, 8 parts........................... Hydrochloric acid, 5 parts..............	From 32 deg. to 27 deg. below zero..	59 deg
Snow, 4 parts........................... Calcium chloride, 5 parts...............	From 32 deg. to 40 deg. below zero..........	72 deg

All the temperatures given above are according to Fahrenheit's scale. By the evaporation of a mixture of solid carbonic acid gas and sulphuric ether, a temperature of no less than 198 deg. F. below the freezing point of water can be produced. Several machines for the production of artificial ice have been invented. Of these perhaps Carre's is the best known. In it the cold is produced by the evaporation of pure ammonia, which has previously been liquefied by pressure.

The production of cold by freezing mixtures depends on the fact that to change bodies from the solid to the liquid, or from the liquid to the gaseous state, *heat* is required. When substances are dissolved, or vaporized, without the application of external heat—as when a salt is dissolved in water—the heat necessary to bring about the change of state is abstracted from the neighboring objects.

Gallic Acid.

Formula, $C_7H_6O_5$: Combining weight, 170.

Gallic acid is prepared from tannic acid by exposing to the air for several months moist powdered nutgalls (which contain nearly half their weight of tannic acid). The dark, mouldy mass so produced is first pressed, and then boiled with water, from which, on cooling, feathery colorless crystals of gallic acid are deposited. It is soluble in one hundred parts of cold or three of boiling water, has an acid, astringent taste, and decomposes when kept in solution.

When heated to 400 deg. F. gallic acid gives off carbonic acid gas, and forms pyrogallic acid. Gallic acid differs from tannic acid in not precipitating gelatine. With ferric salts it forms a black precipitate which disappears when heated. Gallic acid slowly reduces salts of gold and silver to the metallic state, and it is to this property that it owes its introduction into photography.

Gallic acid was used as a developer by the Rev. J. B. Reade, it is said, as early as 1837, and certainly by Fox Talbot, in his calotype process, in 1840. It can also be employed in combination with silver nitrate as an intensifier.

Gelatine.

When a bone is left for a day or two in a weak solution of hydrochloric acid, the mineral part is dissolved away, and a soft mass remains composed of a substance known as *ossein*. An analysis of ossein shows it to be composed in one hundred parts as follows :

Carbon	49.2
Hydrogen	7.8
Oxygen	24.4
Nitrogen	17.9
Sulphur	0.7
	100.0

This ossein is insoluble in either hot or cold water. Other parts of the animal body, as skin, horn, and connective tissue, have the same composition as ossein, and are in all respects similar to it.

But when ossein is boiled with water it undergoes a modification into the substance called *gelatine*, which has somewhat different properties, especially in being soluble in warm water.

In the manufacture of gelatine the raw material—usually the parings of skins, with hoofs, etc.—is treated somewhat differently by different manufacturers. When it is received at the factory it is treated with milk of lime and dried in sheds, so as to stop the decomposition which would otherwise take place. When required for use, the lime is washed off, and, after exposure to the air for two or three days, the skins, etc., are boiled in water until the transformation of ossein into gelatine is complete.

To clarify the hot liquid, either alum or albumen is added, which carries the impurities down to the bottom. The insoluble parts are then removed from the boilers by a strainer or colander, and the liquid gelatine is poured upon tables to solidify, the drying being afterwards completed upon nets.

The gelatine so prepared is a brittle, glassy, transparent mass, which swells up in cold, and dissolves in warm water. When the solution is cold, if it contains more than one per cent. of gelatine, it forms a tremulous jelly. Gelatine is insoluble in alcohol or ether; it is precipitated from its solutions by the addition of excess of alcohol, or by tannic acid, corrosive sublimate, or platinic bichloride. Impure gelatine may be purified by dissolving it in warm water, allowing it to cool, squeezing the jelly so produced through coarse canvas, then washing several times in tepid water (which will remove the coloring matters), dissolving again in warm water, and finally precipitating as a whole clot by the addition of an equal quantity of alcohol.

By long-continued boiling gelatine is changed into a gum-like substance called *metagelatine*, which is soluble in cold water. Boiling with strong alkalies converts gelatine into leucine and glycerine, ammonia being given off.

Chondrin is a very similar substance to gelatine, differing in the fact that it is precipitated by alum, acetate of lead, sulphate of iron, and sulphate of copper.

Gelatine is now of primary importance to the photographer, being used as the vehicle which holds the sensitive salts of silver on the glass plates. When impregnated with about one-sixth its weight of potassium bichromate, the mixture is readily affected by light, and is then insoluble in warm water. This fact is the foundation of most of the photo-mechanical printing processes now employed.

The principal gelatine manufacturers now prepare a special article for photographic work, and this is usually of two qualities, soft and hard. "Nelson's No. 1 Photographic" is a good example of the former, and "Heinrich's" or "Coignet's Gold Label" of the latter. An admixture of the two varieties is best for most purposes.

Isinglass is a superior, and common glue an inferior variety of gelatine. In testing gelatine, each sample is made up into a ten per cent. solution with water, and allowed to cool in a beaker. The beaker is fitted with a lid, through the centre of which passes a stout wire having at its lower end (resting on the gelatine) a half-inch ball, and at the upper end a small tin canister; shot is poured into each canister until the ball is forced into the gelatine, and the weight of shot required in each case indicates the comparative strength of the various samples. In the dry state, gelatine keeps well, but when moist, or in solution, it soon decomposes.

Glass.

Glass is a transparent, hard, brittle, homogeneous solid, formed by melting silica (sand or powdered flint) with oxides of the alkaline, earthy, or common metals. It is insoluble in all acids except hydrofluoric (HF).

There are four principal varieties of glass:

(1) Crown Glass, used for glazing purposes; plate glass is a variety of this; chemically, it consists of silicate of soda and lime.

(2) Bohemian Glass—silicate of potash and lime; this kind of glass is hard to melt, and is, therefore, used for tubes which have to be strongly heated, as, for instance, those employed in the analysis of organic substances.

(3) Flint Glass or Crystal, containing silicate of potash and lead. This is a heavy, lustrous, and easily fusible variety. Our common glass tumblers are usually made of lead glass; and it is practically indispensable for the manufacture of achromatic lenses.

(4) Bottle Glass; silicate of soda and lime, colored green by the presence of oxide of iron. This is the cheapest and most impure variety of glass.

Ordinary glass is rarely colorless, and its tints are due to the presence of small quantities of the oxides of certain metals, especially iron, in the sand which is practically an essential ingredient in the manufacture of every variety of glass.

The colors imparted by these oxides are as follows:

Protoxide of iron (FeO)	green.
Peroxide of iron (Fe_2O_3)	brownish-yellow.
Protoxide of copper (Cu_2O)	ruby.
Peroxide of copper (CuO)	green.
Sesquioxide of chromium (Cu_2O_3)	green.
Oxide of uranium (UO_3)	greenish-yellow.
Oxide of cobalt (CoO)	blue
Oxide of silver (Ag_2O)	lemon to orange.
Oxide of gold (Au_2O_3)	ruby.

By far the commonest impurity is the protoxide of iron (FeO), which stains the glass green. To correct this the manufacturer adds a little black oxide of manganese (MnO_2), which, when heated, readily parts with some of its oxygen. This released oxygen unites with the protoxide of iron, raising it to the state of peroxide (Fe_2O_3), which imparts only a light lemon tint to the glass—a tint which is practically invisible. But, unfortunately, an *excess* of oxide of manganese is almost always added, and under the influence of light this colors the glass a pink or puce color. This is a frequent cause of studios becoming "slower"—exposures lengthened—after they have been erected for some years. On taking out an old pane of glass the difference in color between "that which has been exposed to the light and that which has been protected by the rabbet will often be very noticeable." Fortunately it has been discovered that arsenic trioxide (As_2O_3) will oxidize the iron as effectually as manganese; and as all the arsenic dissipated by heat passes up the chimney of the glass furnace, it leaves no injurious residue.

Lead glass may be known by its blackening all through when heated strongly in a gas flame.

Plate glass is made by pouring melted glass upon a level iron table, and rolling it out to the required thickness with iron rollers; it is then ground and polished.

Sheet glass is made by "blowing" the glass into large cylinders, which are then cut with a diamond and again heated till they open out into flat sheets. "Patent plate" is only sheet glass which has been ground and polished. For large negatives (say sizes above whole-plate) patent plate is to be recommended, as it is, or should be, perfectly flat; and there is thus little danger of breaking the negatives in the printing frame.

The "ruby" glass so largely used by photographers is made by "flashing" (*i.e.*, coating) white glass with a thin layer of glass containing protoxide of copper. Glass colored all through is called "pot metal," and pot metal colored ruby by protoxide of copper is better than the "flashed" glass. But the safety (for photographic purposes) of any sample of red or yellow glass can only be properly tested by the spectroscope, as some varieties of red glass allow many blue rays also to pass.

GLYCERINE.

Formula, $C_3H_8O_3$: Combining weight, 92.

Glycerine is largely obtained, as a bye-product, in the manufacture of soap. For when a fatty body is boiled with a caustic alkali we get soap and glycerine. It is also produced in Wilson's patent process for candle-making, by which fat is decomposed by superheated steam. Glycerine is a viscous, colorless liquid, with a very sweet taste, but no smell. It mixes readily with water, and is neutral to litmus paper. Glycerine is sometimes added to the pyro developer, which it assists in preserving; it also acts as a mechanical restrainer, preventing the too rapid decomposition of the silver sub-bromide or bromide.

GOLD CYANIDES.

When a solution of potassium cyanide is added to a dilute solution of gold trichloride, a yellow precipitate of gold cyanide Au(CN) is produced. The principal solvent of this substance is potassium cyanide in excess, which combines with it to form a double salt—potassium-gold cyanide—which is largely used for gilding by means of the galvanic battery. Copper and silver articles may be gilt by simply making them perfectly clean and then dipping them into the liquid.

GOLD AND SODIUM CHLORIDE.

Formula, $NaAuCl_4+2H_2O$: Combining weight, $361+36=397$.

Prepared by dissolving common salt in a solution of gold trichloride, and evaporating the solution. Yellowish-red crystals of the double salt then appear. When exposed to the air, these crystals effloresce and become yellow. When anhydrous they are red. This salt is also known as sodium chloro-aurate. Prepared in this way, the gold salt keeps better (*i.e.*, is less deliquescent) than if in the form of the pure chloride. When used for toning purposes, a rather larger quantity, by weight, than of the pure gold chloride will, of course, be required.

GOLD.

Symbol, Au: Combining weight, 192.

Gold is found either in detached grains or nuggets scattered through sandy or alluvial deposits, or disseminated in veins or reefs of quartz. Native gold usually contains a little silver. California and Australia yield nine-tenths of the gold now raised annually.

Gold is yellow, lustrous, soft, very malleable and ductile. It reflects yellow light, but very thin gold-leaf transmits green light. Neither oxygen, air, nor steam have any effect upon gold, and it is unaffected by acids, except the mixture of nitric and hydrochloric acids known as aqua regia, in which it readily dissolves to form trichloride of gold, $AuCl_3$.

Gold is too soft for use alone, so that for coins, jewelry, etc., it is alloyed with either copper or silver, or both Pure gold is 24 carats fine, standard gold (employed for coinage) 22 carats, and 18, 15, 12 and 9 carat gold are also recognized. These expressions mean that 24 parts by weight of the alloy contain 22, 18, 15, 12 and 9 parts by weight of pure gold respectively. In the German, American and Italian coinage the standard is 21.6 carats only. English gold coins consist of 11 parts of pure gold alloyed with 1 part of copper.

Gold is precipitated from its solutions by the addition of ferrous sulphate. It then appears as a brown powder, fusible under the blow-pipe, Oxalic acid also slowly reduces gold.

GOLD TRICHLORIDE.

Formula, $AuCl_3$: Combining weight, 302½.

There are two chlorides of gold, the mono-chloride, AuCl, and the terchloride, or trichloride, $AuCl_3$; it is the latter which is exclusively employed in photographic operations. With pure gold there is no difficulty in the preparation of this salt. It is simply necessary to dissolve the gold in about eight times its weight of aqua-regia, an operation which is facilitated by gentle warmth, as by placing the glass vessel in hot water. When the gold is entirely dissolved, the solution must be poured into a small porcelain crucible, and evaporated until the free acid is all, or nearly all, driven off; a few drachms of distilled water may then be added, and the evaporation continued a little longer Lastly, enough distilled water must be added to bring the solution to a standard strength, say one grain of gold to three drachms of water.

Thus, if 20 grains of pure gold were used, enough water should be added to make the whole up to 7½ ounces. The solution of gold trichloride so prepared has a yellow color, and is slightly acid. It should be kept in an opaque bottle, or in a dark place, as light causes it to be decomposed, the gold separating as a brown or black powder.

$AuCl_3$ combines with alkaline chlorides to form double salts called chloro-aurates; thus we have sodium chloro-aurate $NaCl, AuCl_3 + 2H_2O$, and potassium chloro-aurate $KCl, AuCl_3 + 2H_2O$. These are yellow crystalline substances, and it is in this state that chloride of gold is usually sold to photographers, the salts being sealed up in small glass tubes.

It is not at all difficult to make gold trichloride, and a considerable saving may be effected by those who can prepare it for themselves. Pure gold can be obtained by dissolving the substance containing the precious metal in aqua-regia, diluting with water, and then adding ferrous sulphate, which will precipitate the gold as a brown powder, while the other metals will remain in solution. When the brown powder has all settled to the bottom (which takes a long time) the liquid must be poured off, and the gold first washed with distilled water, and then re-dissolved in fresh aqua-regia. The operation can then be continued as described above. But for the purpose of toning prints—the only process in which gold trichloride is required by the ordinary photographer—pure gold is not absolutely necessary, and gold coins may be used without injury to the result. Australian coins are the best, because they contain less copper. Or almost any scraps of broken gold ornaments may be used, and the copper with which the gold is alloyed may either be removed or allowed to remain, as its presence seems to make no difference whatever to the action of the toning solution. A sovereign weighs —or should weigh—113 grains, and will readily dissolve in about ten drachms of hot aqua-regia. Now evaporate the solution down to about four or five drachms (this should be done where there is a good draught, as the acid fumes are injurious), add a little chalk or whiting to neutralize the remaining acid, and filter off the sediment produced; lastly add distilled water to make the whole up to 7½ ounces. The result will be a solution containing 174 grains of terchloride of gold, or two grains of metallic gold to each drachm. As a rule, one grain of gold is sufficient to tone a sheet of sensitized paper. The same quantity of gold purchased in the usual small tubes would have cost 23 shillings (English), besides which there would have been some uncertainty as to getting the true weight and the pure article.

GOLD AND SODIUM HYPOSULPHITE.

Formula, $AuNa_3S_4O_6+2H_2O$: Combining weight, $489+36=525$.

Prepared by gradually mixing concentrated solutions of gold trichloride and sodium hyposulphite, in the proportion of three parts of the former to one part of the latter salt, and then adding alcohol, which precipitates the double hyposulphite of gold and sodium in the form of delicate, colorless needle-like crystals. It has a sweetish taste, and is soluble in water. This substance was formerly known as "sel d'or," and was used to tone the daguerreotype plates employed in the early days of photography.

The silver plate bearing the picture to be toned was covered with a solution of "sel d'or." and was then heated. The double salt was decomposed by the heat, the gold being deposited upon the picture, to which it gave a pleasing color and enhanced durability. Afterwards "sel d'or" was much used for toning silver prints on paper, and we have seen some of these more than twenty years old which still retained their pristine colors.

GUMS.

Gums are vegetable exudations which differ from resins in being soluble in water. Gum arabic may be taken as the type of "gums" generally, its formula being $C_{12}H_{20}O_{10}$. Gum tragacanth is not a true gum, but a mucilage which differs from gum in refusing to dissolve in water, merely swelling up and gelatinizing.

Gums are sometimes used to mount photographs with, but for this purpose they are inferior to either starch-paste or the alcoholic solution of gelatine. In the dry collodion process a weak solution of gum was frequently flowed over the film to act as a "preservative" or "organifier." It was liable, however, to produce a blistering during or after development.

Gum Dammar.

A resin obtained from India and the East Indies. Soluble in alcohol, turpentine, benzole, etc. Used in several varnishes, and as a retouching medium.

Hydriodic Acid.

Formula, HI: Combining weight, 128.

This is a colorless gas, having a pungent smell, and fuming when in contact with air. It is very soluble in water, and is readily decomposed by heat. The gaseous acid is prepared by placing water, potassium iodide, and iodine in a flask, then dropping in small fragments of phosphorus, and heating gently. If an aqueous solution of the acid only be required, the readiest mode is to pass sulphuretted hydrogen through water in which iodine is suspended, and filter off the sulphur which is liberated.

Hydrochloric Acid.

Formula, HCl: Combining weight, 36½.

Pure HCl is a gas, usually prepared by acting on common salt with slightly diluted sulphuric acid. It is very soluble in water. Commercial hydrochloric acid has a yellow tint, owing to the presence of a little iron; the pure aqueous solution is colorless. It fumes when in contact with moist air; and if a glass rod be dipped in liquid ammonia, dense white fumes are seen when it is brought near HCl. But the best test for HCl, or any soluble chloride, is the white precipitate of silver chloride, which is produced by the addition of a drop of a solution of silver nitrate. This precipitate is insoluble in nitric acid, but soluble in ammonia.

Hydrochloric acid was formerly known as *muriatic acid.*

A weak solution of HCl (or, better, of HCl and alum) is very useful as a "clearer," removing the brown stain produced by the action of the pyro developer.

Hydrocyanic Acid (Prussic Acid).

Formula, HCN or HCy : Combining weight, 27.

Hydrocyanic acid is contained in bitter almonds, laurel leaves, etc., and it can be extracted from them by distillation. It is usually prepared by heating dilute sulphuric acid with potassium cyanide in a retort. It is intensely poisonous, so that it is dangerous even to inhale its vapor, and the greatest care should be used in experimenting with it. Hydrocyanic acid was discovered by Scheele, in 1782, and was long known as prussic acid. It cannot be kept for any length of time, but turns brown and decomposes; its odor is very characteristic, resembling that of peach blossoms, or oil of bitter almonds.

Hydrobromic Acid.

Formula, HBr : Combining weight, 81.

For laboratory purposes HBr is prepared by dropping bromine into water containing fragments of phosphorus. It is a colorless gas, very soluble in water.

Hydrofluoric Acid.

Formula, HF : Combining weight, 20.

Prepared by decomposing fluor-spar with sulphuric acid, in platinum or lead vessels. HF is a colorless liquid whose most remarkable property is its power of corroding or etching glass. It must be kept in gutta-percha bottles, or the dilute acid may be preserved in glass bottles coated inside with paraffin. The divisions on thermometers, glass measures, etc., are usually produced by coating the surface with paraffin, scratching off the parts required with a steel point, and then submitting the glass to the action of vapor from hydrofluoric acid placed in a leaden trough.

A dilute solution of HF—about 1 to 20 of water—cleanses glass bottles and plates very effectively. The strong acid is so corrosive that it burns the skin dangerously should it come in contact with it; death has been caused by inhaling the fumes.

A ready method of using this acid to mark glass is to rub up equal parts of barium sulphate and ammonium fluoride in a mortar, adding enough HF to make a paste. Place the whole in a leaden or gutta-percha cup (an egg-cup paraffined over will answer) and add more acid till it is of the consistency of cream. The mixture may now be used with a quill-pen just like ink, leaving it a few minutes on the glass before washing off.

Marks upon glass produced by the action of HF have the great advantage over labels of being indelible. Another use of this substance is that a very weak solution enables gelatine films to be readily stripped from glass.

Hydrochinone.

Formula, $C_6H_6O_2$: Combining weight, 110.

Hydrochinone—whose name has been spelt in many different ways, as hydroquinone, hydrokinone, etc.—is also known as quinol. Like pyrogallol, it is a benzine derivative, and, indeed, it only differs in chemical composition from that well-known substance in containing one atom less of oxygen (Pyro $= C_6H_6O_3$). Hydrochinone occurs naturally in the leaves of the arbutus and certain allied plants. Formerly it war prepared from quinic acid ($C_7H_{12}O_6$) by first converting the latter into kinone ($C_6H_4O_2$), and then treating the kinone with a reducing agent, such as sulphurous acid. It is now obtained far more cheaply by preparing the kinone from aniline by the action of sulphuric acid and potassium bichromate. Hydrochinone forms hexagonal, colorless or slightly yellowish crystals, which are soluble in water, alcohol or ether. It is inodorous, has a sweetish taste, and readily fuses.

In photography hydrochinone was introduced by Abney as a developer in 1880. Its principal advantage over pyrogallic acid is in the fact that it discolors the gelatine plates very little, not absorbing oxygen from the atmosphere so readily. It is suitable for developing either silver bromide or silver chloride films, and for instantaneous work it is especially useful. It does not require the presence of any restrainer, such as ammonium or potassium bromide, and potassium carbonate accompanies it as an accelerator better than ammonia. It should be kept dry, and mixed as required to a strength of from two to four grains per fluid ounce of developer.

Hydrochinone was first prepared by Caventon and Pelletier, in 1820. It melts at 336 deg. F. The substance known as "Permanent Hydroquinone" is sold in lemon-yellow crystals, and contains from $\frac{1}{3}$ to $\frac{1}{2}$ per cent. of sulphurous acid.

HYDRO-SULPHURIC ACID—SULPHURETTED HYDROGEN.

Formula, H_2S: Combining weight, 34.

Hydro-sulphuric acid is certainly better known under its familiar name of sulphuretted hydrogen—or "rotten-egg gas." It is almost always prepared by acting on iron sulphide with dilute sulphuric acid, but the operation should never be conducted in the dark-room, as the gas attacks the silver salts used by photographers.

The most valuable property of sulphuretted hydrogen is its power of combining with, and precipitating as insoluble sulphides, certain of the metals, among which is silver. For this reason photographers use it to recover silver from their residues. The H_2S gas is allowed to bubble through the vessel containing the waste liquids, when any silver which may be present falls to the bottom as a black powder—sulphide of silver. This is removed, dried and fused, when metallic silver is obtained.

Water absorbs about three times its volume of sulphuretted hydrogen, and the solution may be used instead of the gas. It has a poisonous effect when breathed.

HYDROXYL—PEROXIDE OF HYDROGEN.

Formula, H_2O_2: Combining weight, 34.

Hydroxyl is now prepared by dissolving moist hydrated barium peroxide in dilute sulphuric acid, filtering and evaporating *in vacuo* with sulphuric acid. As so obtained it is a colorless, syrupy liquid. It is remarkable in that it is both an oxidizing and a reducing agent. In the former capacity it converts black plumbic sulphide (PbS) into white plumbic sulphate ($PbSO_4$), and is, therefore, useful for cleaning oil paintings in which the white lead has become discolored by the sulphurous fumes from gas, etc. It also bleaches organic matters, changing the color of dark hair to yellow, so that, under the name of "*auricomus*," etc., it is used as a hair-dye.

But hydroxyl is also a reducing agent, depriving certain compounds of the whole or part of their oxygen, when brought into contact with them. In this way it decomposes silver oxide forming silver, water, and oxygen.

In photography, hydroxyl is used for removing the last traces of "hypo" from negatives and prints, which it does by oxidizing the hurtful hyposulphite into the harmless sulphate. Care must be taken, however, not to use too strong a solution, or to leave the objects in too long, or reduction will take place.

HYDROXYLAMINE.

Formula, NH_3O: Combining weight, 33.

This compound, which may be considered as ammonia in which one atom of hydrogen is displaced by a compound atom of hydroxyl, has been prepared from nitric acid by the action of tin and hydrochloric acid. It is a powerful base, and one of its compounds—the hydrochloride of hydroxylamine*—has been proposed by Messrs. Spiller and Egli as a developing agent. Its cost is at present much greater than pyrogallic acid, but it has a great advantage in that it does not stain the gelatine plates. Dr. Divers has prepared hydrochloride of hydroxylamine by the direct action of hydrochloric acid on fulminating mercury, but the process requires to be conducted with great care, and is not one to be practised by the ordinary worker in photography. Still this is the less necessary, as the substance may now be obtained commercially. It seems specially suited for the development of gelatino-chloride films. Its chief drawback is a great tendency to cause "frilling."

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* Also known as hydroxylamine hydrochlorate; its formula is NH_3OHCl.

Hypochlorous Acid.

Formula, $HClO$: Combining weight, $52\frac{1}{2}$.

Only the aqueous solution can be obtained, which is commonly effected by distilling a mixture of one part of nitric acid with two parts of bleaching powder, or by shaking chlorine water up with precipitated mercuric oxide. The solution so obtained is a yellow liquid which possesses powerful oxidizing properties. It also converts silver oxide into silver chloride, oxygen being evolved.

CHAPTER XIII.

CHEMICALS EMPLOYED IN PHOTOGRAPHY (CONTINUED).

IODINE.

Symbol, I: Combining weight, 127.

The elementary body iodine was discovered by Courtois, at Paris, in 1812. He obtained it from kelp—the ashes of certain seaweeds which contain the iodides of sodium and magnesium. Iodine is prepared in a precisely similar way to bromine and chlorine, its fellow-halogens, by heating an iodide—usually potassium iodide—with sulphuric acid and black oxide of manganese. Iodine is slightly soluble in water, more so in alcohol. A few drops of tincture of iodine added to the hydroquinone developer have a powerful accelerating effect, and reduce contrasts.

$$2KI + MnO_2 + 2H_2SO_4 = I_2 + K_2SO_4 + MnSO_4 + 2H_2O.$$

Iodine is usually seen as bluish-black scales, having a somewhat metallic lustre. It melts at 239 deg. Fahr., and at 400 deg. Fahr. is converted into a beautiful violet-colored vapor. Iodine is but very slightly soluble in water, but readily dissolves in alcohol, in carbon-bisulphide, or in chloroform. *Free* iodine forms a blue compound with starch, and this furnishes a well-known test. To make this test, a drop of potassium iodide solution is added to some very dilute starch-paste. If a drop or two of chlorine water is then added to the mixture, some iodine will be liberated, and will unite with the starch to form a blue compound. This blue compound, once formed, is itself a delicate test for "hypo," the latter substance discharging the blue color. A solution of iodine in water can be obtained, if to the water is first added some iodide of potassium. This solution has been recommended by Vogel and by Chapman Jones as a hypo-eliminator. "After fixing as usual, wash the prints in three or four changes of water, and then place them in water colored by the iodine solution to about the tint of pale sherry, and replace this iodine water with fresh as may be necessary, until the prints show a slight but persistent blue color. This blue is especially visible on the back, and shows excess of iodine, and therefore absence of hypo. To get rid of the blue color, rinse the prints in a solution of sulphite of soda and carbonate of soda, made very weak indeed (a few drops of a strong solution to a pint or a quart of water), and then wash them in two or three changes of clean water, and dry. The iodine solution must not be used in a metallic vessel."

IRIDIUM TETRA-CHLORIDE.

Formula, $IrCl_4$: Combining weight, 335.

Iridium is an intensely hard metal which is found in small quantities mixed with platinum. It is now used to make the indestructible points of pens. There are three chlorides of iridium, but the most interesting is the tetra-chloride, which is produced by dissolving finely divided iridium in aqua regia, heating, and evaporating to dryness. The $IrCl_4$ so obtained is a black, deliquescent, amorphous substance which dissolves in water, forming a reddish-yellow solution. It combines with ammonium to form ammonium chlor-iridiate. An aqueous solution of the latter salt is naturally of a pale-yellow color, but when exposed to light it becomes white, and then changes to purple, violet, and lastly assumes a beautiful blue tint.

IRON ACETATE.

Formula, $Fe(C_2H_3O_2)_2+4H_2O$: Combining weight, 246.

There are two acetates of iron, ferrous acetate, which has the formula given above, and ferric acetate, $Fe_2(C_2H_3O_2)_6$. It is the ferrous salt—the protacetate of iron—which is used in photography.

When iron is dissolved in acetic acid and the solution evaporated *in vacuo*, greenish-white crystals of ferrous acetate, very soluble in water, are produced. It can also be obtained by acting on sugar of lead (lead acetate) with carbonate of iron; or by the combination of ferrous sulphate (green vitriol) and calcium acetate. Under the name of "black liquor," or "iron liquor," ferrous acetate is largely used as a mordant in calico-printing. Dr. Just (in his book on "Gelatine Emulsion Papers," 1890) recommends ferrous acetate as a good developer for gelatino-chloride papers.

Iron Ammonium Citrate.

Prepared by dissolving two parts of freshly precipitated ferric hydrate in three parts of citric acid, and passing ammonia through the mixture until it is saturated. On evaporating, a yellowish mass of ammonia-citrate of iron will be obtained, which is insoluble in strong, but soluble in weak alcohol of 40 per cent.

Iron Ammonium Sulphate.

Formula, $FeSO_4, (NH_4)_2SO_4+6H_2O$: Combining weight, $284+108=392$.

Prepared by dissolving 38 parts of ferrous sulphate with 33 parts of ammonium sulphate in the minimum quantity of hot water. When the solution is filtered and allowed to crystallize it forms transparent bluish-green crystals, which are soluble in five parts of cold or two of hot water. It is a very stable substance, and hence is frequently used instead of ferrous sulphate for analytical purposes.

(Iron): Ferric Nitrate.

Formula, $Fe_2(NO_3)_6$: Combining weight, 484.

Ferric nitrate is formed by dissolving iron in nitric acid. On evaporating the solution it deposits colorless crystals which contain a large amount (12 or 18 molecules) of water of crystallization. These crystals deliquesce rapidly in air, and dissolve in water to form a brown liquid, which is decomposed by boiling.

(Iron): Ferric Oxalate.

Formula, $Fe_2(C_2O_4)_3$: Combining weight, 376.

Prepared by dissolving ferric hydrate ($Fe_2(HO)_6$) in a solution of oxalic acid. It is very soluble in water. Its use in photography depends mainly on the fact that by exposure to light it is reduced to ferrous oxalate. The paper employed in the platinotype printing process is prepared with ferric oxalate.

(Iron): Ferric Sulphate.

Formula, $F_2(SO_4)_3+9H_2O$: Combining weight, $404+162 = 566$.

Ferric sulphate can be prepared by oxidizing ferrous sulphate with nitric acid. Ten parts of the ferrous salt are dissolved in water with four parts of sulphuric acid, and nitric acid is then added to the hot solution. On evaporation, the anhydrous ferric salt is obtained as a white powder.

(Iron): Ferrous Bromide.

Formula, $FeBr_2+6H_2O$: Combining weight, $216+108 = 324$.

A solution of ferrous bromide can be made by dissolving iron in hydrobromic acid. By evaporating this solution, green crystals of the salt can be obtained.

(Iron): Ferrous Chloride.

Formula, $FeCl_2$. Combining weight, 127.

Prepared by dissolving iron in hydrochloric acid and evaporating *in vacuo*, when bluish-green crystals having the composition $FeCl_2+4H_2O$ are obtained. These deliquesce and decompose in air. They are very soluble in water and in alcohol.

(Iron): Ferrous Iodide.

Formula, FeI_2+4H_2O: Combining weight, $310+72 = 382$.

Prepared by digesting iron filings and iodine in water. When the colorless aqueous solution so obtained is exposed to air it decomposes; but this may be prevented by the addition of a little sugar. On evaporation, green crystals of ferrous iodide containing four equivalents of water are obtained. The anhydrous salt can be obtained by heating iron filings with iodine in a closed porcelain crucible.

(IRON): FERROUS NITRATE.

Formula, $Fe(NO_3)_2+6H_2O$: Combining weight, $180+108 = 288$.

Prepared by adding barium nitrate to ferrous sulphate and evaporating *in vacuo.* The crystals so obtained are very soluble in water. This salt is very unstable, quickly absorbing oxygen and passing into ferric nitrate.

(IRON PERCHLORIDE): FERRIC CHLORIDE.

Formula, Fe_2Cl_6: Combining weight, 325.

Perchloride of iron, or ferric chloride, is obtained by dissolving peroxide of iron (Fe_2O_3) in hydrochloric acid. The solution is yellow when dilute, reddish-brown when concentrated. By passing chlorine over red-hot iron wire, brilliant red crystals of anhydrous perchloride of iron are produced. These are very soluble in water, alcohol, or ether.

(IRON PROTOSULPHATE): FERROUS SULPHATE.

Formula, $FeSO_4+7H_2O$: Combining weight, $152+126 = 278$.

Protosulphate of iron, or ferrous sulphate, is commercially known as copperas, or green vitriol. The pure salt can be obtained by dissolving pure iron wire in sulphuric acid, but it is made on a large scale by exposing heaps of moistened iron pyrites (FeS_2) to the action of the air. As usually seen it consists of green crystals, readily soluble in water, almost insoluble in alcohol. All the ferrous compounds combine readily with oxygen, and when ferrous sulphate is left in contact with air, as in a partly filled bottle of the aqueous solution, the salt absorbs oxygen and is converted into ferric sulphate. The change is indicated by the alteration of color from green to yellowish-brown. It may be retarded or prevented by adding two or three drops of sulphuric acid, or by keeping a little clean iron wire in the bottle. The bottle should also be kept quite full and well corked.

Ferrous sulphate was introduced as a developing agent by Robert Hunt, in 1844. It was commonly employed both in the calotype and in the collodion process. As an ingredient for making the ferrous oxalate developer, ferrous sulphate is still largely used.

KAOLIN (CHINA CLAY).

Formula, $Al_2Si_2O_7+2H_2O$: Combining weight, 258.

Kaolin, or China clay, is a silicate of alumina, produced by the disintegration of the feldspar which is an essential ingredient of all granites. It is an extremely fine white powder, which is frequently used to clear, or decolorize, solutions of nitrate of silver, such as the negative bath in the wet collodion process, which have become brown, owing to the presence of albumen or other organic matter. It is a natural product, known also as China clay or porcelain clay, occurring plentifully in regions where granitic rocks abound.

LEAD ACETATE.

Formula, $Pb(C_2H_3O_2)_2+3H_2O$: Combining weight, 378.

Prepared by dissolving litharge (lead monoxide) in acetic acid. From its appearance and its sweet (though also astringent) taste, lead acetate is commonly known as *sugar of lead.* The crystals are soluble in a little more than their own weight of water; soluble also in alcohol. The aqueous solution is frequently milky, from the presence, or formation, of lead carbonate. Lead acetate was found a useful addition, by the early experimenters, to the gallic acid they used for developing pictures on paper. By its use the details of the picture were brought out more rapidly and more clearly. Lead acetate has also been recommended as a hypo eliminator. Added to the ordinary fixing bath it gives prints a blackish tone.

LEAD CHLORIDE.

Formula, $PbCl_2$: Combining weight, 242.

Prepared by dissolving lead oxide or carbonate in hydrochloric acid. It is but slightly soluble in cold, though more so in hot, water, from which (on cooling) it is deposited in white silky needles.

LEAD FERROCYANIDE.

Formula, $Pb_2Fe(CN)_6+3H_2O$: Combining weight, $624+54=678$.

A white precipitate of lead ferrocyanide is formed when a solution of potassium ferrocyanide is mixed with one of lead nitrate. The salt parts with its water of crystallization when heated. It is insoluble in water; partly soluble in hot ammonia; very soluble in a hot solution of ammonium chloride.

LEAD NITRATE.

Formula, $Pb(NO_3)_2$: Combining weight, 330½.

Prepared by dissolving litharge (PbO) in hot dilute nitric acid. On cooling and evaporating, milk-white octahedral crystals of lead nitrate are obtained. It is soluble in water; but very slightly soluble in alcohol.

LITHIUM BROMIDE.

Formula, LiBr : Combining weight, 87.

Prepared by dissolving lithium carbonate, or lithia (Li_2O) in hydrobromic acid. It is very soluble in water or alcohol.

LITHIUM CARBONATE.

Formula, Li_2CO_3 : Combining weight, 74.

Metallic lithium was discovered by Arfvedson in 1817. The carbonate is made by adding ammonium carbonate to lithium chloride. It is only slightly soluble in water; but the solution acts as a powerful accelerator to pyrogallol as a developer.

Lithium Iodide.

Formula, $LiI+3H_2O$: Combining weight, 134+54 = 188.

The elementary body, lithium, was discovered in 1817, though the pure metal was not isolated till 1855, by Bunsen. It is the lightest known solid. Although very rare in any quantity, yet minute traces of the salts of lithium occur almost everywhere in water, soil, animals and plants. The principal lithium compound which has been used in photography is lithium iodide, which may be obtained by dissolving lithium hydrate or carbonate in hydriodic acid. Another method is to mix strong solutions of calcium iodide and lithium sulphate, evaporate to dryness, and treat the residue with alcohol, which will dissolve out the lithium iodide. The long, slender crystals of lithium iodide are so very deliquescent, and the pure salt is so expensive, that it has not come into use for iodizing collodion, for which it is otherwise well suited, being more readily soluble in alcohol than the iodide of potassium generally employed.

Magnesium.

Symbol, Mg: Atomic weight, 24.

Metallic magnesium is a silvery, lustrous metal, which soon tarnishes in moist air. It is manufactured in large quantities from the chloride, and is chiefly sold as "ribbon," "wire," or in the powdered state. It has a great affinity for oxygen, and when it is ignited (which may be effected by simply holding it in the flame of a candle) it produces a bluish-white light of dazzling brilliancy. This magnesium light is very rich in actinic rays, and hence it has been largely used for photographing dark interiors, as caves, etc., and for photography at night. Bunsen and Roscoe found that while the light-giving value of direct sunlight is 524 times greater than that of burning magnesium, its chemical value is only 36 times as great. A burning magnesium wire about one-twenty-sixth of an inch in thickness gives as much light as 74 stearin candles weighing five to the pound.

A convenient lamp is sold which pushes out the metallic ribbon as fast as it is consumed, and so maintains a fairly constant light. A substitute for this is to use a few inches of a narrow tin tube—a pea-shooter, for instance—and pass the ribbon through it. The tube can be held in the hand, and the ribbon pushed through steadily while it burns at the far end. The white smoke produced is *magnesia*, *i.e.*, magnesium oxide.

The latest development of the magnesium light in photography is its use in the form of powder, either alone or spread upon gun-cotton, or mixed with oxidizing substances, such as chlorate of potash. Fifteen grains of the powdered metal intimately mixed with half its weight of gun-cotton, and burnt at a distance of six or eight feet from the sitter, will give a flash of such brightness that an instantaneous portrait can be readily secured.

MAGNESIUM BROMIDE.

Formula, $MgBr_2$: Combining weight, 184.

This substance is found in sea water and in saline springs. It is deposited as needle-shaped crystals, having the composition $MgBr_2+6H_2O$, when magnesia is heated in hydrobromic acid. By heat, these crystals are decomposed into the substances from which they were produced.

MAGNESIUM CARBONATE.

Formula, $MgCO_3$: Combining weight, 84.

Magnesium carbonate occurs in nature as the mineral called *magnesite.* It is soluble in water saturated with carbonic acid gas, the solubility increasing rapidly with the pressure.

The *magnesia alba* of druggists is a mixture of several complex carbonates of magnesium. It is a bulky white powder soluble in ammoniacal solutions.

MAGNESIUM CHLORIDE.

Formula, $MgCl_2$: Combining weight, 95.

Prepared by evaporating magnesia dissolved in hydrochloric acid to which an equal weight of sal-ammoniac has been added, and then fusing the mixture. It is a white deliquescent substance, very soluble in water; all but insoluble in alcohol. Magnesium chloride is used in preparing chloride of silver emulsions; it has also been tried as a fixing agent for silver prints, in the place of hypo.

MAGNESIUM IODIDE.

Formula, MgI_2: Combining weight, 278.

This substance occurs in sea water, and in brine springs. It can be prepared by dissolving magnesia in hydriodic acid. It forms crystals which deliquesce in air, and decompose when heated, iodine being liberated.

MAGNESIUM NITRATE.

Formula, $Mg(NO_3)_2+6H_2O$: Combining weight, $148+108 = 256$.

This salt occurs in the mother-liquor from the saltpetre manufacture. It can be prepared by dissolving *magnesia alba* in nitric acid. Its prismatic crystals deliquesce in air. They are soluble in half their weight in water; soluble also in alcohol.

MAGNESIUM SULPHATE.

Formula, $MgSO_4+7H_2O$: Combining weight, $120+126 = 246$.

Magnesium sulphate is familiarly known as "Epsom salts," from its occurrence in the water of a mineral spring at Epsom. It is now chiefly obtained from a mineral called *keiserite*, which occurs in layers in the salt-beds at Stassfurt. It is usually sold as a white crystalline powder, which is very soluble in water, but insoluble in alcohol.

The addition of Epsom salts to the fixing-bath is found to check, or prevent, the "frilling" to which certain dry-plates are more or less subject.

MERCURY (QUICKSILVER).

Symbol, Hg: Combining weight, 200.

Mercury, whose symbol, Hg, is derived from the name *hydrargyrum* applied to it by Pliny, is commonly called quicksilver. It is found, combined with sulphur, as *cinnabar* (mercuric sulphide), in the famous mines of Almaden in Spain, Idria in Carniola, and in California. The mercury of commerce usually contains small quantities of other metals, as iron, lead and zinc. It may be freed from these by distillation, or by treatment with dilute nitric acid.

Pure mercury is a silvery-white metal, freezing at —103 deg. Fahr., and boiling at 575 deg. Fahr. It combines with many of the other metals to form alloys which are called amalgams.

Mercury volatilizes at all temperatures, but of course the rapidity of volatilization increases as the temperature increases. It is on this fact that its use as a developer in the daguerreotype process depends. The exposed silver plate is placed over a dish of warm mercury, and the latter metal combines with those parts of the plate which have been affected by light.

[The volatilization of mercury at ordinary temperatures may be well shown by putting a little mercury in a test-tube, inserting a loose plug of cotton-wool in the top of the tube, and then suspending it in a large vessel full of sulphuretted hydrogen. A deposit of mercury sulphide will slowly form around *the top* of the tube.]

MERCURY BICHLORIDE.

Formula, $HgCl_2$: Combining weight, 271.

Bichloride of mercury, or mercuric chloride, is familiarly known as corrosive sublimate. It is usually prepared by heating a mixture of mercury sulphate and common salt. Its colorless crystals are soluble in fifteen parts of cold or two of hot water. The addition of a little ammonium chloride to the cold water increases its power to dissolve the mercury salt. It is soluble in alcohol and in ether, and is a violent poison.

In photography, corrosive sublimate is largely used for intensifying. The thin negative is soaked in a saturated solution until it turns white (owing to the formation of calomel

(Hg_2Cl_2) and silver chloride), and then in a weak solution of ammonia until black.

MERCURY SUB-CHLORIDE.

Formula, Hg_2Cl_2: Combining weight, 471.

Mercury sub-chloride, or mercurous chloride, is the *calomel* of druggists. It is prepared by heating mercury with mercury bichloride. It is insoluble in water, alcohol, and cold dilute acids. When exposed to light it turns gray, owing to the separation of metallic mercury.

MERCURY IODIDE.

Formula, HgI_2: Combining weight, 454.

Mercuric iodide is formed when solutions of potassium iodide and of mercuric chloride are mixed together. It appears first as a yellow precipitate, but this rapidly changes to scarlet. It is soluble in excess of either of the solutions from which it is formed, more especially in excess of potassium iodide.

Mercuric iodide, followed by ammonia, forms an excellent intensifier for gelatine negatives.

There is also a *mercurous iodide*, Hg_2I_2, which is formed by mixing solutions of potassium iodide and mercurous nitrate. It is of a greenish-yellow color.

MERCURY MON-OXIDE.

Formula, HgO: Combining weight, 216.

Mercury mon-oxide is also called mercuric oxide, red oxide of mercury, or red precipitate. It can be obtained by heating mercury to a temperature rather below its boiling point for several weeks in a glass flask with a long neck. Commercially, it is prepared by heating a mixture of mercury and mercuric nitrate. It is usually seen as a bright red crystalline powder, but it can be obtained of an orange-yellow hue by adding caustic soda to a solution of a mercuric salt. Mercury mon-oxide is a poisonous substance, slightly soluble in water.

When heated it darkens, but resumes its original tint on cooling. By strong heat, it is broken up into mercury and oxygen.

NAPHTHA.

True naphtha is a hydro-carbon which occurs naturally as "*mineral naphtha*" in the rocks of Pennsylvania and Canada, and less abundantly in certain parts of Europe and Asia.

Coal naphtha is a nearly identical substance, obtained by distillation from coal during the manufacture of coal-gas. Naphtha is a clear, limpid, oily liquid, which burns with a bright, smoky flame. It will not mix with water, but is a good solvent for caoutchouc (india-rubber).

Owing to its freedom from oxygen, it is used to protect the metals sodium and potassium from the air, the bottles in which they are preserved being kept full of naphtha.

The term "wood naphtha," or "vegetable naphtha," is sometimes applied to "wood spirit" (methyl alcohol), but this is a misapplication, as the latter is a very different substance.

NITRIC ACID.

Formula, HNO_3: Combining weight, 63.

Nitric acid—often called *aqua fortis*—is prepared by distilling potassium nitrate with strong sulphuric acid.

Commercial nitric acid has a yellow color, owing to the presence of nitric peroxide; the pure acid is colorless. The yellow color can be destroyed by blowing air through the acid. It is a very corrosive liquid, producing dangerous wounds if it comes in contact with the skin. The dilute acid colors the skin, nails, clothes, etc., of a bright yellow color. Nitric acid is a very powerful oxidizing substance—that is, it readily parts with some of its oxygen to other bodies. It attacks all ordinary metals, except gold and platinum, forming a series of salts called nitrates, which are soluble in water.

Nitric acid fumes strongly when exposed to the air, and has an irritating odor. It can be distinguished from other acids by the red fumes which are given off when it is poured on copper.

NITRO-HYDROCHLORIC ACID—AQUA-REGIA.

Neither nitric nor hydrochloric acid alone is able to dissolve gold or platinum. Yet a mixture of these acids—to which the name of *aqua-regia* has been given—readily dissolves either of these "noble" metals. The reason is that by the mixing of the acids *chlorine* is set free, and this nascent chlorine unites with the metals to form chlorides, which are soluble.

The mixture should be made in the proportion of one of nitric to three of hydrochloric acid, and, to lessen the violence of the action, an equal quantity of water may be added.

NITROUS ACID.

Formula, HNO_2: Combining weight, 47.

This is a very unstable substance, prepared by passing nitrous anhydride into water. Sometimes it acts as a reducing agent, precipitating gold and mercury from solutions; at others it exhibits oxidizing properties, liberating oxygen and becoming reduced to nitric oxide and water. Nitrous acid forms a series of salts called *nitrites*, which behave similarly to the acid, but are much more stable. These nitrites can be distinguished from *nitrates* by the reddish fumes they evolve when treated with dilute acids.

OIL OF LAVENDER.

Oil of lavender—an inferior variety of which is sold as "oil of spike"—is made by distilling lavender flowers with water. It is a yellowish liquid, soluble in alcohol, but insoluble in water. In photography it has been used for dissolving bitumen and pyroxyline, for scenting certain pastes or cerates used in burnishing, and in varnishes.

OXALIC ACID.

Formula, $C_2H_2O_4 + 2H_2O$: Combining weight, $90 + 36 = 126$.

Oxalic acid, combined more especially with potassium, occurs plentifully in the vegetable kingdom, as in the leaves of the wood-sorrel, the stalks of rhubarb, etc. It is now made in large quantities by the action of caustic potash on sawdust; but for experimental purposes, a small quantity is best prepared by acting upon sugar or starch with nitric acid.

Oxalic acid is not very soluble in cold water, but more so in warm water and in alcohol. The solution is very poisonous, and, as the crystals are much like those of Epsom salts, it has been the cause of many accidents. The best remedy is the administration of powdered chalk suspended in water.

Oxalic acid is much used in calico printing, and for taking ink stains out of linen. It is also employed for cleaning brass and leather.

When crystallized, it forms prisms, whose composition is $C_2H_2O_4+2H_2O$. By heating to 212 deg. Fahr., the water of crystallization is driven off, and a white powder remains. Oxalic acid forms two classes of salts called normal or alkaline oxalates, and acid oxalates. The former are all soluble, the latter generally insoluble, in water.

OZONE.

Symbol, O_3: Molecular weight, 48.

In 1840, Schönbein showed that ozone is an allotropic form of oxygen. Each molecule of ordinary oxygen contains two atoms, while in the molecule of ozone three atoms are crowded together, so that any volume of ozone weighs half as much again as the same volume of oxygen.

Ozone is now usually produced by submitting oxygen to the silent electrical discharge. It may be detected by the blue coloration which it produces in paper that has been dipped first into starch paste and then into potassium iodide solution.

Ozone is a very powerful oxidizing agent, releasing readily its third atom of oxygen. Thus both silver and mercury, upon which oxygen has little or no effect, are quickly tarnished by ozone.

Holmes' ozone bleach is a substance sold commercially (it is an alkaline hypochlorite), which is an effective reducer for over-dense negatives.

PALLADIUM AND ITS COMPOUNDS.

Palladium is a metal often found associated with platinum. Its formula is Pd, and atomic weight 107. Like platinum it forms two series of chlorides, $PdCl_2$ and $PdCl_4$. Palladium bichloride, $PdCl_2$ is a dark-brown powder which forms double salts by combining with alkaline chlorides in a similar manner to the corresponding platinum compounds. Of these double salts the chloro-palladite of potassium ($PdCl_2,2KCl$) has been used in photography for toning prints, transparencies, and enamels.

PARA-AMIDOPHENOL.

Formula, $C_6H_4NH_2OH$: Combining weight, 109.

Many organic compounds possess the property of reducing salts of silver to the metallic state. But as photographic developers only those are of use which will reduce salts of silver *that have been exposed to light*, while leaving intact *non-exposed* salts. The latter class are comparatively limited in number; but to Dr. Andresen, of Berlin, we owe an addition to this class in the form of the substance known as para-amidophenol, which is chemically related to hydrochinone and to eikonogen. It was introduced by him in 1891 as a brownish crystalline powder, slightly soluble in cold water, more so in hot water.

But by the aid of acids, salts are obtained from para-amidophenol which are easily soluble in water. As an example we have hydrochloric para-amidophenol—$C_6H_4NH_2HClOH$—which, combined with carbonate of potash, makes a good developer.

By the action of caustic soda we get para-amidophenol-natrium—$C_6H_4NH_2ONa$; and by the action of caustic potash we obtain para-amidophenol-potassium—$C_6H_4NH_2OK$; these two alkaline compounds are easily dissolved even by cold water.

RODINAL is the name given to a concentrated solution of one of the above forms of para-amidophenol. It is a reddish-brown liquid which requires diluting with from fifty parts (for negatives) to one hundred parts (for bromide paper) of water for use.

PHOSPHORIC ACIDS.

There are three distinct substances, to each of which the term "phosphoric acid" has been more or less frequently applied.

Meta-Phosphoric Acid, HPO_3, combining weight 80, is produced when phosphoric anhydride (P_2O_5), the white powder produced by burning phosphorus in oxygen, is dissolved in cold water.

Phosphoric Acid, H_3PO_4, combining weight 98, is best obtained by distilling nitric acid with amorphous phosphorus. It is used in photography in Willis' aniline process for the copying of plans.

Phosphoric acid forms a series of salts called phosphates, which are distinguished by the *yellow* precipitate they give with solutions of silver nitrate.

Pyro-Phosphoric Acid, $H_4P_2O_7$, combining weight 178, is obtained—as the name implies—by heating phosphoric acid until water is driven off.

PHOSPHORIC (OR ORTHO-PHOSPHORIC) ACID.

Formula, H_3PO_4: Combining weight, 98.

This acid can be prepared by heating red phosphorus in a retort with common strong nitric acid. On a large scale it is made by dissolving bone-ash in sulphuric or hydrochloric acid. In commercial phosphoric acid, arsenic acid is frequently present as an impurity.

Pure phosphoric acid forms colorless crystals, which are very soluble in water. The solution tastes intensely sour, and reddens blue litmus. It is not poisonous. The best test for phosphoric acid is molybdate of ammonia, an acid solution of which is turned yellow by phosphoric acid. When heated to a dull red in a platinum crucible, phosphoric acid is converted into a transparent mass of meta-phosphoric acid—HPO_3; this is the *glacial phosphoric acid* of druggists.

By long continued heat phosphoric acid may be changed finally into another modification, called pyro phosphoric acid—$H_4P_2O_7$.

A solution of the ordinary, or ortho-phosphoric, acid is used in Willis' aniline process. Dr. Maddox finds that the addition of a trace of phosphoric acid to the ordinary pyro-ammonia developer, improves the color of the image and tends to prevent fog.

Photo-Salts.

During the year 1887, Mr. Carey Lea, of Philadelphia, published, in the *American Journal of Science*, the results of a long series of researches upon the nature of the change effected by light upon the haloid salts of silver. Previously, Mr. Lea had been the principal advocate of the theory which states that "the first effect produced by light is simply a physical change, predisposing the elements of the silver haloid to dissociation, so that when a reducing agent (the developer) is applied, the molecules so affected yield more quickly to its influence."

The other, or chemical theory of development, declared that the effect of light was to remove some of the haloid element—the chlorine, bromine, etc.—combined with the silver, leaving a sub-salt, which was readily reduced by the developer:

$2AgCl$	$=$	Ag_2Cl	$+$	Cl
Silver Chloride	*yields*	Silver Sub-chloride	and	Chlorine.

Mr. Lea's later researches have led him to believe in a modification of this chemical theory. He finds that light decomposes a small part of the silver salt, *and that the sub-salt then forms a molecular combination with the unaltered salt.* To such a molecular combination Lea applies the name of a "photo-salt," and speaks of "photochloride of silver," or "photobromide of silver," as the the case may be. The proportion of the "sub-salt" in the combination may vary from a very minute quantity up to eight or nine per cent. These photo-salts exhibit a wide range of coloration, from white through pink, and purple to black. The typical photochloride of silver is of a magnificent red hue. It is possible that the way to "photography in colors" lies through these photo-salts. A very important part of Mr. Lea's discovery lies in the fact that he has been able to prepare these photo-salts chemically, without the action of light.

PLATINUM.

Symbol, Pt : Combining weight, 194.

Platinum is found only in the metallic state. Grains and nuggets of this metal occur in the sands of rivers in the Ural Mountains, Borneo, California, etc. It is a white, very malleable and ductile metal, which never tarnishes, since platinum does not combine directly with oxygen at any temperature.

No single acid can dissolve platinum, but aqua-regia, or any liquid capable of evolving chlorine will attack it. The high fusing-point of platinum—about 4,000 deg. Fahr.—and its power of resisting chemical action, specially fit it for use in the chemical laboratory, and render it serviceable to the photographer. Platinum crucibles, basins, spatulas, foil, and wire are frequently required. Platinum crucibles should never be put naked into a coke or charcoal fire, but always placed within a covered earthen crucible. They should never be used for melting any of the oxides of a readily fusible metal, such as lead or tin, as these metals will combine with the platinum and form an alloy, and the vessel will be destroyed.

PLATINUM TETRACHLORIDE (PLATINIC CHLORIDE).

Formula, $PtCl_4 + 5H_2O$: Combining weight, $336 + 90 = 426$.

Prepared by dissolving platinum in aqua-regia and evaporating several times, each time adding hydrochloric acid. A compound having the formula $PtCl_4$, 2HCl is thus obtained, from which the hydrochloric acid may be expelled by heat. Platinic chloride forms red crystals, which are soluble in water, producing an orange-colored solution. When strongly heated, platinic chloride parts with two atoms of chlorine and is reduced to platinous chloride, $PtCl_2$. Platinic chloride combines with other chlorides, especially those of the alkali metals, to form a series of double chlorides, which vary greatly in their solubility. Potassium platinic chloride ($PtCl_4$, $2KCl$), for example, is insoluble in water, while sodium platinic chloride ($PtCl_4$, $2NaCl$), is readily soluble. The former salt —more generally known, perhaps, as potassium chloroplatinite —is largely used in the platinotype process.

POTASSIO FERRIC OXALATE.

Formula, $Fe_2(C_2O_4)_3, 3K_2C_2O_4$: Combining weight, 874.

This constitutes the green crystals seen at the bottom of a hot-bath platinotype solution after it has been used several times; it is also found in the old ferrous oxalate developer. It is soluble in water; insoluble in alcohol. It is decomposed by light, and hence is used in certain "blue" processes.

POTASSIUM.

Symbol, K: Atomic weight, 39.

Metallic potassium was first obtained by Davy, in 1807. He decomposed caustic potash by a strong current of electricity, and obtained a silvery-white, soft metal, which tarnished instantly on exposure to air, owing to its great affinity for oxygen. For this reason potassium is usually kept under some liquid which contains no oxygen, as petroleum. Potassium decomposes water at all temperatures, forming potassium hydrate (caustic potash), and liberating hydrogen, the energy of the chemical combination being sufficient to inflame the escaping hydrogen.

POTASSIUM BICHROMATE.

Formula, $K_2Cr_2O_7$: Combining weight, 294.

The chromium compounds are obtained by heating chrome iron ore with potash carbonate, by which means a soluble yellow chromate, K_2CrO_4, is formed. When sulphuric acid sufficient to combine with half the potassium in the yellow salt is added, the *bichromate* of potash is formed, and crystallizes out in large red crystals as the solution cools. Potassium bichromate dissolves in ten parts of cold water, but is much more soluble in hot water. It is insoluble in alcohol, and is very poisonous.

When bichromate of potash is mixed with an organic substance, such as gelatine, and exposed to light, it becomes dark-colored, owing to the liberation of oxygen, and the consequent reduction of the bichromate to chromic oxide, Cr_2O_3. A further effect is that the gelatine is rendered insoluble in water, and non-absorbent. Advantage is taken of this in the carbon printing process in photography, powdered carbon being mixed with the bichromatized gelatine, which is then exposed to light beneath a negative, and finally washed in hot water. The portions unacted on by light are dissolved away, while the insoluble parts remain to form the picture. Potassium bichromate has a very injurious effect upon the skin if there be any cuts or scratches through which it can enter.

POTASSIUM BROMIDE.

Formula, KBr: Combining weight, 119.

Prepared by dissolving bromine in caustic potash, whereby a mixture of bromide and bromate of potash is produced. This is evaporated down to dryness, and gently ignited to drive off the oxygen, by which the bromate is reduced to bromide also. Potassium bromide forms clear cubical crystals, which are readily soluble in water, slightly soluble in alcohol. It is a favorite restraining agent in the ordinary pyro developer, preventing any action upon the silver bromide which has not been affected by light, and steadying and regulating the decomposition of that which has.

POTASSIUM CARBONATE.

Formula, K_2CO_3: Combining weight, 138.

Carbonate of potassium was formerly known as salts of tartar, "potashes," or "pearl-ash." The original source of this potassium salt was the ashes which resulted from the burning of wood or other vegetable matter. When such ashes were boiled in pots the carbonate of potassium was extracted from them, and it was then easily obtained in the solid state by evaporating the water.

Of late years much has been obtained from beet-root, and from the potassium sulphate, which occurs in such vast deposits at Stassfurt in Germany.

The "pearl-ash" of commerce contains small quantities of sodium carbonate, and potassium sulphate, etc. Potassium carbonate is a white deliquescent substance, very soluble in water, but insoluble in alcohol. Owing to its affinity for water, it is employed in removing the last traces of water from alcohol. It is a strongly alkaline salt.

"Potash"—as K_2CO_3 is familiarly called—is largely used to render alkaline the pyro developer. It must be carefully distinguished from the acid potassium bicarbonate (bicarbonate of potash), $KHCO_3$.

POTASSIUM CHLORATE.

Formula, $KClO_3$: Combining weight, 122½.

Chlorate of potassium can be made by passing chlorine into a strong solution of caustic potash or of potassium carbonate. It is now largely manufactured by passing chlorine into milk of lime and then adding potassium chloride.

Chlorate of potassium forms flat, shining crystals having an acid and cooling taste, like nitre.

When heated to about 670 deg. Fahr., these crystals decompose and all the oxygen is liberated; hence this salt is largely used as a source of oxygen gas. By mixing with the chlorate of potassium one-fifth of its weight of black oxide of manganese, the heat required to liberate the oxygen is greatly reduced. One pound of the salt should produce four cubic feet of oxygen. As the commercial chlorate always contains small quantities of chlorine, the oxygen gas should be purified by passing it through two wash-bottles partly filled with water, in which a little caustic potash or potassium carbonate has been dissolved, before it is allowed to enter the bag in which it is to be stored.

POTASSIUM CHLORIDE.

Formula, KCl: Combining weight, 74½.

Chloride of potassium is much like rock-salt in appearance and properties. Thick beds of potash-salts occur near Stassfurt, probably formed by the drying up of some old lake or inland sea. It forms colorless cubes, which are soluble in three parts of cold water; more soluble in hot water, but insoluble in alcohol.

POTASSIUM CITRATE.

Formula, $K_3H_5C_6O_7$: Combining weight, 306.

Made by adding carbonate of potassium to a solution of citric acid until the latter is neutral; then evaporate to dryness. Citrate of potassium is a white crystalline powder which deliquesces when exposed to the air. It is very soluble in water; insoluble in alcohol. It acts as a preservative of ordinary sensitized paper; being either mixed with the silver bath or the paper may be floated upon it after silvering. It also acts as a powerful restrainer in alkaline development.

POTASSIUM CYANIDE.

Formula, KCN (or KCy): Combining weight, 65.

Prepared by fusing dry ferrocyanide of potassium with potassium carbonate in an iron crucible.

The iron separates and sinks to the bottom, when the liquid potassium cyanide can be poured off, and, being allowed to cool, solidifies to a white cake, which can be broken up for use. Owing to imperfect mixture or fusion, potassium carbonate is frequently present, as an impurity, in the commercial salt; but its presence is not directly harmful.

Cyanide of potassium emits an odor of prussic acid, and gives off that substance freely when any acid is added to it; it is highly poisonous. The aqueous solution dissolves gold and silver, forming double cyanides, which are largely used for electro-gilding and electro-plating. Potassium cyanide was largely used as a fixing agent during the "wet-collodion epoch" of photography, but for gelatine plates it has been displaced by hyposulphite of soda.

POTASSIUM FERRICYANIDE (RED PRUSSIATE OF POTASH).

Formula, K_3FeCy_6: Combining weight, 329.

Prepared by passing chlorine gas through a solution of potassium ferrocyanide; the latter loses one atom of potassium and is converted into the ferricyanide. This salt forms beautiful red crystals, which are soluble in two and one-half parts of cold, or one and one-half of boiling water; insoluble in alcohol.

Potassium Ferrocyanide (Yellow Prussiate of Potash).

Formula, $K_4FeCy_6 + 3H_2O$: Combining weight, $368 + 54 = 422$.

Prepared commercially by heating nitrogenous organic matter—as horn, hide-parings, etc.—with potashes and iron filings. The fused mass is heated with water, which, on evaporation, then yields tough yellow crystals. It is soluble in four parts of cold, or two parts of hot water; insoluble in alcohol.

Potassium Fluoride.

Formula, KF: Combining weight, 58.

Fluoride of potassium is made by neutralizing hydrofluoric acid with caustic potash. The cubical crystals have a saline taste and deliquesce in air.

Potassium Hydrate (Caustic Potash).

Formula, KHO: Combining weight, 56.

Caustic potash—or "potash," as it is sometimes termed—is formed when metallic potassium is placed in water. It is usually prepared by adding slacked lime (calcium hydrate) to a rather weak hot solution of potassium carbonate. Chalk is formed, which sinks to the bottom, and the clear liquid is decanted and evaporated to dryness, when the caustic potash remains as a hard, white, brittle solid. Lastly, it is fused, and cast into sticks, in which state it is usually sold.

Potassium hydrate is a powerful alkali, burning the skin, and neutralizing acids. It is largely used in soap-making. Since it is very deliquescent the sticks should be kept in a stoppered bottle. Caustic potash dissolves in about half its weight of water. Caustic potash works admirably with hydrochinon as a developer for gelatine dry plates.

POTASSIUM IODIDE.

Formula, KI: Combining weight, 166.

Prepared by digesting iodine with water and iron filings, and then adding potassium carbonate. It crystallizes in cubes which are very soluble in water, slightly soluble in alcohol. The pure salt should be neutral, but, as usually met with, it has an alkaline reaction. The aqueous solution dissolves iodine freely.

POTASSIUM META-BISULPHITE.

Formula, K_2SO_3, SO_2: Combining weight, 222.

This salt may be obtained by passing sulphurous anhydride in excess into a solution of potassium carbonate, and adding alcohol. Care must be taken to keep the sulphurous anhydride in excess, or else the normal sulphite will be formed. The meta-bisulphite of potash was introduced in 1887 by Messrs. Mawson & Swan as a preservative of pyro when in solution.

POTASSIUM NITRATE.

Formula, KNO_3: Combining weight, 101.

Nitrate of potassium, familiarly known as "nitre," or "saltpetre," forms a surface-deposit on the soil of many hot countries, as Bengal, Egypt, etc. It is also prepared by mixing solutions of sodium nitrate and potassium chloride.

Potassium nitrate is soluble in five parts of cold, and in its own weight of hot water. It contains nearly half its weight of oxygen, with which it readily parts when heated with any combustible substance. For this reason nitre is much used in the manufacture of gunpowder and fireworks.

Potassium chloride is frequently present in ordinary nitre. Its presence may be detected by the white precipitate produced by the addition of a few drops of silver nitrate.

POTASSIUM NITRITE.

Formula, KNO_2: Combining weight, 85.

Potassium nitrite can be produced by heating the nitrate until part of its oxygen is driven off. This decomposition takes place more readily when some oxidizable metal, such as lead, is present.

Nitrite of potash forms small, white crystals, which deliquesce in air, and are insoluble in absolute alcohol.

The use, in photography, of KNO_2 depends mainly on the fact that it is a halogen absorbent. Bromide paper, treated with a solution of potash nitrite, forms an excellent actinometer. The paper should be soaked for ten minutes in a ten per cent. solution, and allowed to dry slowly in the dark. In strong sunlight, such paper will attain its deepest color—indigo blue—in twenty-five seconds.

POTASSIUM OXALATE.

Formula, $K_2C_2O_4+2H_2O$: Combining weight, $176+36 = 212$.

The *neutral* oxalate of potash (which is the salt employed by photographers) is prepared by neutralizing oxalic acid with potassium carbonate. It crystallizes in transparent prisms, which dissolve in three parts of water. When heated, the crystals part with their water of crystallization and become white and opaque. The binoxalate, or acid oxalate of potash, can be distinguished by the sour taste of its crystals; its formula is C_2HKO_4. It is also known as *salt of sorrel*, from its occurrence in that plant.

The neutral potassium oxalate is employed in the preparation of ferrous oxalate, which is largely used as a developer for paper negatives and transparencies, and—chiefly on the Continent—for gelatine dry-plates also. It is also much used in the platinotype printing process.

POTASSIUM PERMANGANATE.

Formula, $KMnO_4$: Combining weight, 158.

Permanganate of potash is made by pouring boiling water on potassium manganate, and then filtering through asbestos or glass wool. Its prismatic crystals are red by transmitted, but black by reflected light. It is soluble in sixteen parts of water, and the solution—sold as "Condy's Fluid"—is a well-known disinfectant. Potassium permanganate is a useful oxidizing agent.

POTASSIUM SULPHATE.

Formula, K_2SO_4: Combining weight, 174.

Potassium sulphate is largely produced as a bye-product, in the manufacture of bichromate of potash and certain other substances. It forms colorless crystals, which dissolve in ten parts of cold or four of boiling water.

POTASSIUM SILVER CYANIDE.

Formula, $KAg(CN)_2$: Combining weight, 200.

This substance crystallizes in feathery tufts or hexagonal prisms. It is soluble in four parts of water, and is unaffected by light.

POTASSIUM SULPHIDE.

Formula, K_2S: Combining weight, 110.

Potassium and sulphur combine in several proportions, of which the mono-sulphide, K_2S, is perhaps the best known. It can be made by dividing a saturated solution of caustic potash into two parts, passing sulphuretted hydrogen through one part and then adding the other half. It is an alkaline, caustic body.

POTASSIUM SULPHO-CYANIDE.

Formula, $KS(CN)$: Combining weight, 97.

Prepared by heating yellow prussiate of potash with carbonate of potash and sulphur, and boiling the mass with alcohol. It is a transparent, crystalline substance, very soluble in water. When five parts of the salt are dissolved in four parts (by weight) of water, a temperature of —4 deg. Fahr. is produced. Sulpho-cyanide of potassium has been used as a fixing agent, especially for positive pictures, in place of hyposulphite of soda. It is present in human saliva, a fact which may affect the permanency of photographs that have had the tongue passed over them (a common practice) in order to induce the glossy surface to take tints or colors more readily. It is also used in the toning-bath for gelatino-chloride and collodio-chloride prints.

PRIMULINE.

Primuline is the "trivial" name of a yellow dye obtained by the action of sulphur upon toluidine, a coal-tar base closely allied to aniline. It was discovered by Mr. A. G. Green in 1887, and was first used as a dye for calico, one of its peculiarities being that it requires no mordant. Its photographic properties were announced at the British Association meeting at Leeds in 1890. The chemical composition of primuline is very complex and is perhaps hardly known with certainty. Primuline itself is not sensitive to light, but by treatment with nitrous acid it is converted into diazo-primuline which, when in contact with cotton, linen, paper, etc., is rapidly affected by exposure to the sun. Further, the diazo-primuline has the power of combining with phenols or amines to form brightly colored compounds; but after exposure to light it loses this power. It is therefore possible to secure colored prints upon calico, etc., in the following manner: (1) Soak the calico in a solution of primuline, then rinse and soak in a solution of nitrous acid. (2) Dry the calico and expose it to light beneath a positive. (3) Develop by soaking the exposed calico in one of various solutions according to the color desired, as resorcin (orange), betanaphthol (red), phenol (yellow), etc.; finally, rinse and dry. The process gives a positive from a positive; or a negative picture from a negative.

PRUSSIAN BLUE; $\mathrm{FE_4(FECY_6)_3}$.

There are several varieties of this useful substance, which is largely employed in painting. When a ferric salt is added to potassium ferrocyanide a blue precipitate of *soluble Prussian blue*, $\mathrm{Fe_4K_2Cy_{12}}$, is produced. This substance dissolves in pure water, but is insoluble in saline solutions. By adding ferric chloride to a solution of soluble Prussian blue a deep blue powder is precipitated, which is *insoluble Prussian blue*, Fe_7Cy_{18}, and this is the ordinary, or commercial article. It is sold in cubical dark-blue lumps, and is insoluble in water and in weak acids. It is soluble in oxalic acid, forming a dark-blue liquid, which is used as an ink.

PYROCATECHIN.

Formula, $C_6H_4(OH)_2$. Combining weight, **110**.

Also known as catechol, and as brenzcatechin. Has the same relative composition as hydroquinone and resorcin; but the atoms in the molecule are differently arranged. This substance is sold in whitish crystals, which are soluble in water and in alcohol. It forms a fairly good substitute for pyrogallol in the alkaline development of dry plates.

PYROGALLIC ACID (PYROGALLOL).

Formula, $C_6H_6O_3$: Combining weight, **126**.

Pyrogallic acid—as the name implies—is prepared from gallic acid by the action of heat. The gallic acid may be placed in a porcelain crucible, over the top of which a piece of blotting-paper is then tied, the whole being covered and surmounted by a paper cone. With a Bunsen burner, or spirit-lamp, the temperature is then raised to 350 deg., when the gallic acid is decomposed into pyrogallic acid—which rises through the pores of the blotting-paper and settles on the inside of the paper cap—and carbonic acid gas, which escapes. The great drawback to this, and indeed to most methods of preparing the substance, is that a large part of the gallic acid is decomposed into metagallic acid, $C_6H_4O_2$, so that only about one-fifth of the gallic acid is converted into pyrogallic acid.

An improvement introduced by Liebig is to mix powdered pumice with the gallic acid, and pass a slow stream of carbonic acid gas over the mixture so as to remove the pyrogallic acid before it has had time to become over-heated. By this method the yield is nearly doubled, but is still less than half the possible amount. For an experiment on a small scale the best method is that devised by Professor Thorpe, of heating gallic acid in glycerine (150 grains to each ounce) in a glass retort. The temperature of the liquid must not rise above 400 deg. Fahr. The heat drives off carbonic acid gas, and a solution of pyrogallic acid in glycerine is left behind, which will "keep" for months. For preparing "pyro" on a large scale, an aqueous solution of gallic acid is heated to 400 deg. Fahr. in a closed vessel for thirty minutes. The solution is then boiled with animal charcoal, filtered and evaporated to dryness. The solid residue so obtained is then distilled by gently heating it in a vacuum. In this way nearly all the gallic is converted into pyrogallic acid.

Pyrogallic acid has not the characteristic properties of an acid—it has a bitter, not a sour taste; and it does not redden blue litmus—hence chemists do not consider it a true acid, and in chemical text-books it is now termed "pyrogallol," but it is familiarly known to photographers as "pyro."

Pyrogallol forms brilliant crystalline plates, which break up into a fine feathery powder, so light as to be scattered by a breath. It is extremely soluble in water, alcohol and ether. It melts at 239 deg. Fahr., and when the liquid boils it gives off a colorless, irritating vapor. Aqueous solutions of pyro abstract oxygen from the atmosphere, and from the air dissolved in ordinary water, quickly turning brown and becoming useless to the photographer. The addition of a little citric or nitric acid retards this change. A solution of pyro in glycerine and alcohol keeps fairly well. When the solution of pyro is rendered alkaline, it becomes first yellow and then brown, a fact which distinguishes it from gallic acid, which undergoes no such changes. With solutions of pure ferrous salts pyrogallol gives a fine blue tint, which the least trace of a ferric salt changes to green.

Pyro is an active reducing agent, absorbing oxygen so eagerly that it decomposes most of the salts of the "noble metals"—gold, silver, and platinum. For this reason it has been in constant use in photography for the last forty years; and its price has been reduced as the demand for it became greater, from 10*s.* or 15*s.* per ounce, to a shilling or even less.

Owing to its power of absorbing oxygen, pyrogallic acid is always used for that purpose in gas analysis.

PYROXYLINE.

Formula, $C_{18}H_{22}(NO_2)_8O_{15}$: Combining weight, 846.

When cotton wool is steeped in a mixture of equal parts of strong nitric and sulphuric acids the formidable explosive known as *gun-cotton* ($C_{18}H_{21}(NO_2)_9O_{15}$) is produced, which is quite insoluble in any mixture of alcohol and ether. But when the acids are mixed in the proportion of three parts of sulphuric to one of nitric, and a certain quantity of water—say seven-eighths of a part—is added, then the cotton which is immersed in the mixture acquires different properties. It is not explosive, and it is soluble in a mixture of alcohol and ether. Either cotton-wool, straw, paper, pitch, flax (as linen) or calico, etc., may be used, but in each case the resulting product will be slightly different. When paper is used the resulting product is known as *papyroxiline.* The chemical composition of each of these substances is $C_6H_{10}O_5$, which may be regarded as six atoms of carbon combined with five molecules of water ($H_{10}O_5 = 5H_2O$). The sulphuric acid combines with the water, which is invariably present in even the purest nitric acid, and the anhydrous nitric acid is then able to attack the cotton, displacing either two or three of its atoms of hydrogen and replacing them by an equal number of nitrosyl (NO_2) groups. The presence of nitrogen tetroxide in the altered cotton may be proved by the red fumes which are seen when the cotton is ignited in a glass globe exhausted of air.

Potassium nitrate (KNO_3) may be used instead of nitric acid, the latter being then formed by the action of the sulphuric acid on the potassium nitrate.

RESORCIN.

Formula, $C_6H_4(OH)_2$: Combining weight, 110.

Prepared by a complex process from benzole and sulphuric acid. Is soluble in water and in alcohol. Resorcin is isomeri in composition with hydroquinone and with catechol; and some experimenters say that it may be used similarly in the composition of an alkaline developer. But Dr. Andresen finds that *pure* resorcin has no effect upon silver bromide, and attributes its supposed developing powers to the fact that traces of its isomers were present in the samples used by those who noted its (supposed) developing powers.

SALICYLIC ACID.

Formula, $C_7H_6O_3$: Combining weight, 138.

Prepared by passing carbonic acid gas through a heated mixture of caustic soda and carbolic acid. Soluble in 700 parts of cold, or 9 parts of boiling water, or in 4 of alcohol. Is a powerful germicide, and a few drops of the solution added to any mountant, or to solutions of alum or of citric acid, will prevent decomposition.

SHELLAC.

A resinous substance deposited by an insect upon the twigs of plants in India, etc. The crude "lac" as imported is known as "stick-lac," since it includes the pieces of wood, etc., upon which the insect deposited the resin. The "lac" is freed from the wood by rolling, grinding and washing, and is then called "seed-lac." When the seed-lac is melted and cast into thin layers, it is called "shellac," or "button-lac" if cast into sticks. By dissolving shellac in caustic soda, and passing chlorine through the solution, the natural brown or red color of the lac is removed, and we then get "bleached lac."

Shellac is soluble in alcohol, especially if a little oil of lavender be added. In photography it is much used as a varnish for negatives; but it should have about five per cent. of sandarac added to it, in order to make it dry as a smooth level sheet.

SILVER.

Symbol, Ag. (from *argentum*). Atomic weight, 108. Specific gravity, $10\frac{1}{2}$. Melting point, 1900 degrees Fahrenheit.

The alchemists called silver *Luna* or *Diana*, from its white color, like that of the moon. In nature, silver is found pure or "native" in Peru, Norway, etc., and its ores are not uncommon.

It is a very malleable and ductile metal, and is the best conductor known of heat and of electricity. Pure silver is too soft for use in the arts, so that it is usually alloyed with copper. The "standard silver" of which our silver coins are made contains 92½ per cent. of silver and 7½ per cent. of copper.

The best solvent for silver is dilute nitric acid, but boiling strong sulphuric acid will also dissolve it.

In photography, silver was much used in the daguerreotype process, by which photographs were produced on thin plates of silver supported by a copper backing. The purity and cleanliness of the surface of the silver plate are of the highest importance in this process.

Silver is not affected by pure air, oxygen or water; but ozone and sulphuretted hydrogen cause it to tarnish. Silver hooks are frequently employed to raise the plates from the developing solution, and in the collodion process the plate rests, in the dark slide, upon silver wire.

Silver, when melted, absorbs or *occludes* several times its volume of oxygen from the air.

When the metal solidifies this oxygen is forced out, giving the peculiar arborescent appearance often noticed on masses or buttons of pure silver, and which is known as the "silver tree." During 1890–91 Mr. Carey Lea showed that silver could exist in several "allotropic" states, being then sometimes of a yellow, sometimes of a blue color, and possessing distinct properties.

SILVER ACETATE.

Formula, $C_2H_3AgO_2$: Molecular weight, 167.

Silver acetate is formed (1) by addition of silver nitrate to a strong solution of an acetate; (2) by dissolving silver carbonate in hot acetic acid. It is an exception to most of the acetates in that it requires 100 parts of water to dissolve one part of the salt.

Silver acetate forms white flat crystals. Carbonate of silver is frequently present, as an impurity, in commercial silver acetate.

Silver Ammonio-Nitrate.

Formula, $AgNO_3 + 2NH_3$. Combining weight, 204.

If ammonia is added to a neutral solution of silver nitrate until the precipitate produced is barely re-dissolved, and the solution then allowed to evaporate, fine bright prismatic crystals of ammonio-nitrate of silver will be produced.

Plain salted paper may be advantageously sensitized with this salt, but it is unsuited for albumenized paper, as the ammonia dissolves the albumen.

Silver Bromide.

Formula, $AgBr$: Molecular weight, 188.

Silver bromide is found native in very small quantities in Mexico, Chili, and Brittany. It may be prepared by the direct combination of its elements, as in the daguerreotype process, where a plate of silver is exposed to the vapor of bromine. In the collodion and gelatine processes of photography silver bromide is formed by the action of silver nitrate upon a soluble bromide, as:

$AgNO_3$	$+$	NH_4Br	$=$	NH_4NO_3	$+$	$AgBr$
Silver Nitrate	*combines* *with*	Ammonium Bromide	*to* *form*	Ammonium Nitrate	*and*	Silver Bromide.

When hydrobromic acid is added to solutions of silver salts, silver bromide is precipitated. It is a yellowish-white substance which alters to gray on exposure to light, a change which is retarded or altogether stopped by the presence of even a trace of nitric acid or free bromine. Silver bromide is insoluble in water, but soluble in alkaline hyposulphites, cyanides, sulpho-cyanides, and in ammonia.

The different modifications of silver bromide, which are sharply distinguished by their relative sensitiveness to light, also present certain physical differences which are indicated in the following table: *

By Transmitted Light.		ByReflected Light.	Occurrence.
Semi-transparent.	Orange.	Slate blue.	In fresh collodion emulsion.
		Bluish-white.	Older bromide of silver in collodion wet-plates.
		Bluish-white.	In very sensitive wet collodion plates.
	Reddish-orange.	Yellowish-white.	In very old bromide of silver in collodion.
Almost opaque.	Violet-blue.	Yellowish-white.	Very sensitive collodion emulsion.
		Greenish-yellow.	Bromide of silver in gelatine; sensitiveness medium.
		Green, or violet-green.	Very sensitive gelatine emulsion.
	Blue.	Indistinct.	Slightly sensitive silver bromide in collodion, yielding indistinct pictures. Affected by red end of spectrum.

Silver Carbonate.

Formula, Ag_2CO_3: Combining weight, 276.

This is a yellowish-white powder formed by adding an alkaline carbonate to a solution of silver nitrate. It is soluble in ammonia and dilute acids; slightly soluble in water.

When exposed to light, or heated, silver carbonate darkens. It is decomposed by heat into silver oxide and carbonic acid gas. Silver carbonate in solution has an alkaline reaction, turning red litmus blue.

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* De Pitteurs, *Chem. Centr.* 1884, p. 411.

SILVER CHLORIDE.

Formula, $AgCl$: Combining weight, 143.5.

Silver chloride occurs in waxy, translucent masses called "horn-silver" in the mines of Mexico, Peru, Chili, and the Harz Mountains. It is also obtained as a curdy-white precipitate when hydrochloric acid, or any soluble chloride, is added to a solution of a silver salt.

For example, the paper used in printing the ordinary positive pictures in photography is coated with silver chloride, which is produced by floating the paper (previously impregnated with ammonium or sodium chloride) upon a solution of silver nitrate:

$NaCl$	$+$	$AgNO_3$	$=$	$AgCl$	$+$	$NaNO_3$
Sodium Chloride	*combines with*	Silver Nitrate	*to form*	Silver Chloride	*and*	Sodium Nitrate.

Pure silver chloride is white, but under the influence of light it darkens, passing through various tints of violet until it becomes black.

Silver chloride is insoluble in water and dilute acids. It is dissolved by sodium hyposulphite, ammonia, potassium cyanide, and by strong solutions of alkaline chlorides and mercuric nitrate. Silver sub-chloride (Ag_2Cl) has recently been prepared by M. Guntz. He first obtains silver sub-fluoride (Ag_2F) by heating powdered silver with a solution of silver fluoride; and then changes this into the sub-chloride by the addition of hydrochloric acid.

SILVER CHROMATE.

Formula, Ag_2CrO_4: Combining weight, $332\frac{1}{2}$.

This compound may be obtained by adding a solution of potassium bichromate or chromate to a solution of silver nitrate. A reddish-brown precipitate is produced, which is silver chromate; this may be filtered off, washed, and dried. It dissolves in hot dilute nitric acid, and separates out on cooling in small ruby-red crystalline plates. Paul Roy used silver chromate in the preparation of an emulsion in 1881 (see *British*

Journal Photo. Almanac, 1882), and W. K. Burton (*Almanac*, 1888), points out that it might be used (from its deep ruby color) to prevent halation, and also as the actual sensitive salt in an emulsion.

SILVER CITRATE.

Formula, $Ag_3C_6H_5O_7$: Combining weight, 513.

May be obtained as a white precipitate by adding silver nitrate to sodium citrate.

It is insoluble in water, but boiling water decomposes it, with separation of silver.

SILVER FLUORIDE.

Formula, AgF: Combining weight, 127.

Prepared by dissolving silver oxide or carbonate in hydrofluoric acid, and evaporating the solution. It is readily soluble in water (in which it differs from the haloid salts of silver) and even deliquesces by absorption of water from the atmosphere.

SILVER HYPOSULPHITE.

Formula, $Ag_2S_2O_3$: Combining weight, 328.

This compound—more correctly called silver thiosulphate—is a snow-white powder, obtained by adding dilute silver nitrate to a strong solution of sodium hyposulphite. The precipitate is contaminated with silver sulphide, from which it may be separated by dissolving in ammonia. On carefully neutralizing the ammoniacal solution with nitric acid, the silver hyposulphite is again thrown down.

It has a sweet taste, is but slightly soluble in water, and is —in the moist state—very unstable, decomposing into silver sulphide and sulphuric acid.

With hyposulphite of soda the silver hyposulphite combines to form two double salts. The first of these—$AgNaS_2O_3$—is produced when the silver salt is in excess; it is nearly insoluble in water. The second—$Ag_2Na_4(S_2O_3)_3$—is formed when there is an excess of the soda; it is very soluble in water. In all fixing operations it must clearly be our aim to produce the second (or soluble) salt.

SILVER IODATE.

Formula, $AgIO_3$: Combining weight, 283.

Prepared by adding potassium iodate to silver nitrate.

SILVER IODIDE.

Formula, AgI : Combining weight, 235.

Silver iodide is very rare as a mineral, but it is readily prepared by adding potassium iodide to a solution of a silver salt. In the daguerreotype process, it is prepared by the direct combination of its elements, a plate of silver being exposed to the vapor of iodine.

$$\underset{\text{Silver}}{Ag} \underset{\textit{combines with}}{+} \underset{\text{Iodine}}{I} \underset{\textit{to form}}{=} \underset{\text{Silver Iodide.}}{AgI}$$

Unlike silver bromide and chloride, the iodide is insoluble in ammonia, which, however, turns it white; its normal color being yellow. When heated, the yellow color deepens. Pure silver iodide is not affected by light, but in the presence of a little silver nitrate, or any other iodine absorbent, the silver iodide darkens, becoming first brown and then grayish-black.

SILVER NITRATE.

Formula, $AgNO_3$: Combining weight, 170.

Silver nitrate can be made by dissolving silver in an equal weight of nitric acid, adding water and evaporating the solution, when the salt appears as colorless crystals, having a specific gravity of $4\frac{1}{3}$. They are soluble in their own weight of cold water, the solution being neutral. Silver nitrate is known in surgery as *lunar caustic*, and is used to destroy proud flesh, etc. It is very poisonous. Pure silver nitrate is not affected by light unless organic matter be present, when it speedily darkens.

Silver nitrate is very largely used in photography, and it is fortunate that it can be purchased at a price but little exceed-ing the value of the silver which it contains. The reason of this is that the salt is produced, as a bye-product, in the separation of gold from silver by the refiners. But very cheap silver nitrate is almost certain to contain impurities—such as copper, and organic matter—whose presence would spoil the salt for photographic purposes. To remedy this the suspected crystals should be dissolved in distilled water, and the liquid evaporated. The *re-crystallized* salt will be pure.

Enormous quantities of silver nitrate are used in the manufacture of our modern gelatine dry-plates. The great English makers of these dry-plates usually buy the silver nitrate in quantities of ten thousand ounces at a time.

To find the exact amount (without calculation) of silver nitrate required to combine with the soluble bromide which is added to it to make an emulsion, Mr. W. Ackland has invented a very useful form of slide-rule.

SILVER NITRITE.

Formula, $AgNO_2$: Combining weight, 154.

Silver nitrite is best obtained by mixing equal parts of strong warm solutions of silver nitrate and potassium nitrite. The salt produced is a white crystalline powder, difficultly soluble in cold water, soluble in hot water with partial decomposition. By a moderate heat it is decomposed into silver, silver nitrate and nitric oxide. $AgNO_2$ has been added to the silver nitrate bath used in the wet-collodion process with advantage as regards increased sensitiveness and density of the wet-plate, but with disadvantage as regards the production of fog.

SILVER OXIDE.

Formula, Ag_2O: Combining weight, 232.

Silver oxide may be prepared by adding potassium hydrate to silver nitrate. It is a brownish-black powder, one part of which dissolves in three thousand parts of water, the solution being alkaline. Silver oxide should be kept in water in an opaque bottle. Treatment with strong ammonia converts it into *fulminating silver*, a highly explosive substance.

Silver oxide is used in the collodion process to neutralize a too acid bath of silver nitrate. It has also been employed to separate copper oxide from silver nitrate.

SILVER PHOSPHATE.

Formula, Ag_3PO_4: Combining weight, 419.

This substance is thrown down as a yellow powder when silver nitrate is added to any normal alkaline phosphate. It is insoluble in water, but dissolves in nitric acid and in ammonia. It blackens when exposed to light, and becomes red when heated.

SILVER SODIUM-HYPOSULPHITE.

Formula, $AgNaS_2O_3+2H_2O$. Combining weight, 243+36=279.

This salt—more properly called silver sodium-thiosulphate—can be prepared by adding an excess of a neutral solution of silver nitrate to a solution of hyposulphite of soda, when it appears as a brown precipitate. It is but slightly soluble in water.

If, on the contrary, an excess of a solution of hyposulphite of soda be added to a solution of silver nitrate or chloride, no precipitate will be produced, for a compound of silver and sodium will then be formed which is very soluble in water. Its formula is $Ag_2Na_4(S_2O_3)_3$. This is the salt which is, or ought to be, formed in all fixing operations, whether of negatives or prints. Any given quantity of hyposulphite of soda is able to dissolve about one-third of its weight of silver chloride. If less of the hypo be employed, the *insoluble* double salt will be formed, and will appear as small crystals on the surface of the paper or glass.

SILVER SULPHATE.

Formula, Ag_2SO_4: Combining weight, 312.

Prepared by dissolving silver in hot strong sulphuric acid, or by dissolving silver nitrate or carbonate in dilute sulphuric acid. Silver sulphate forms small lustrous crystals which dissolve in two hundred parts of cold or sixty-eight parts of hot water. The addition of a little sulphuric or nitric acid to the water much increases the solubility.

SILVER SULPHIDE.

Formula, Ag_2S: Combining weight, 248.

This compound, formerly known as sulphuret of silver, occurs as a mineral called *silver glance.* It can be made by fusing together silver and sulphur, and is precipitated as a black powder when sulphuretted hydrogen is passed into solutions of silver salts. It is insoluble in water and ammonia, but soluble, with decomposition, in nitric acid, by which it is converted into sulphate and nitrate of silver.

SODIUM.

Symbol, Na: Combining weight, 23.

Metallic sodium was first obtained by Davy, in 1807, by decomposing caustic soda by a strong current of electricity. Sodium is never found naturally in the free state, but in combination with other substances it is one of the most widely diffused of the elements. It is a silvery metal, which has so great an affinity for oxygen that it tarnishes immediately on exposure to the air. Similarly it decomposes water to obtain oxygen. A rough but sure test for sodium and its compounds is the golden yellow color they produce when placed in the colorless flame of the Bunsen burner or spirit-lamp. Recent improvements by Mr. H. Y. Castner have reduced the price of sodium from five shillings to about one shilling per pound. He prepares a carbide of iron by coking iron with pitch, and mixes this with fused caustic soda. When this mixture is heated the metallic sodium distills over. The process is being worked on a large scale at Oldbury, near Birmingham, Eng., and the sodium is used in the manufacture of aluminium.

SODIUM ACETATE.

Formula, $NaC_2H_3O_2+3H_2O$: Combining weight, $82+53=136$.

Prepared by the action of dilute acetic acid on sodium carbonate. Commercially it is made by adding soda to pyroligneous acid. It dissolves in three parts of cold or one of boiling water; in absolute alcohol it is almost insoluble. Sodium acetate forms large, colorless prismatic crystals, which do not deliquesce like those of potassium acetate. It is much used in the preparation of the gold acetate bath for toning prints.

SODIUM BICARBONATE.

Formula, $HNaCO_3$: Combining weight, 84.

Natural deposits of this salt are found in Africa, where it is called *trona*, and in South America, where it is known as *urao.* It can be prepared by passing carbonic acid gas into a saturated cold solution of the normal carbonate, Na_2CO_3. The bicarbonate of soda is a crystalline white powder, soluble in about ten parts of water, and with a feebly alkaline taste and reaction.

SODIUM BI-BORATE (BORAX).

Formula, $Na_2B_4O_7+10H_2O$: Combining weight, $202+180=283$.

Borax has been in use from very ancient times as a flux. In chemical analysis it is used to detect certain metals by the characteristic colors which their oxides impart to "borax beads." Borax is now made by boiling crude boric acid (obtained from certain lagoons in Tuscany) with sodium carbonate. It is soluble in twenty parts of cold or six of boiling water, and the solution has an alkaline reaction.

In photography, borax is used in the preparation of a toning-bath for prints.

SODIUM BROMIDE.

Formula, $NaBr$: Combining weight, 103.

Prepared by neutralizing hydrobromic acid with sodium carbonate. From hot solutions it crystallizes in anhydrous cubes; from solutions below 90 deg. Fahr. in prismatic crystals, containing two molecules of water—$NaBr+2H_2O$. It is freely soluble in water and in alcohol.

SODIUM CARBONATE.

Formula, $Na_2CO_3+10H_2O$: Combining weight, $106+180=286$.

Immense quantities of *soda ash* are produced annually in South Lancashire—the alkali district—by treating salt with sulphuric acid, and then heating the product (sodium sulphate) with powdered coal-slack and chalk.

From the *black ash* so produced, the impure sodium carbonate (*soda ash*) is dissolved out with water.

It is then purified by dissolving again in water, and re-crystallizing, when large transparent crystals—called *soda crystals*—of sodium carbonate are obtained. These are largely used to soften the water employed for washing clothes, etc. The crystals dissolve in two parts of cold, or in less than their own weight of boiling water. The solution has a strongly alkaline taste and reaction. In the United States, washing-soda crystals are known as "sal soda."

As the alkaline ingredient of the pyro developer, carbonate of soda is, by many photographers, preferred to ammonia. It should be purchased at the chemist's as "pure carbonate of soda in crystals." It is also sold as a dry white powder—"exsiccated carbonate of soda"—which is much stronger, because the water of crystallization ($10H_2O$) has been driven off by heat.

SODIUM CHLORIDE (COMMON SALT).

Formula, $NaCl$: Combining weight, $58\frac{1}{2}$.

Common salt occurs plentifully in nature in sea water, in salt springs, and as rock salt. When the chemically pure sodium chloride is required, it is made by passing hydrochloric acid gas into a solution of common salt; or by neutralizing the same acid with carbonate of soda. Sulphate of sodium and magnesium chloride are the most common impurities. Sodium chloride crystallizes in cubes. It is almost equally soluble in hot and in cold water, but is insoluble in alcohol.

A little common salt—about one ounce to each pound of chlorate of potash—is useful in making oxygen for lantern work. It appears to cause the gas to be given off more regularly.

SODIUM HYDRATE (CAUSTIC SODA).

Formula, $NaHO$: Combining weight, 40.

This salt is formed when sodium is dissolved in water, but most of that used in commerce is obtained as a bye-product in the manufacture of sodium carbonate.

Sodium hydrate is a white, fibrous solid. It melts below a red heat, without decomposition, and is usually cast into sticks for sale. It is a powerful alkali, and is largely used in soap making.

SODIUM HYPOCHLORITE.

Formula, $NaOCl$: Combining weight, 74½.

This substance is difficult or impossible to obtain in the pure state, but it is contained in the bleaching liquid formed by passing chlorine into caustic soda. This liquid was formerly known as *Eau de Labarraque.* An easier method of preparing it is to dissolve four ounces of sodium carbonate in ten ounces of hot water; and two ounces of hypochlorite of lime (commonly called "chloride of lime," or bleaching powder) in thirty ounces of water; and then mix the two solutions, boil, and filter.

When carbonate of potash is used, practically the same result is obtained, but the liquid is then known as "Javelle water," or *Eau de Javelle.* Exactly the same quantities of each substance may be used. These solutions should be kept in stoppered bottles. They are useful for removing all traces of sodium hyposulphite from negatives or prints. For this purpose about half an ounce of either solution should be mixed with twenty ounces of water.

SODIUM HYPOSULPHITE ("HYPO").

Formula, $Na_2S_2O_3+5H_2O$: Combining weight, 15890+=248.

Some acids contain sulphur in place of oxygen. In recent times these acids have been distinguished by the prefix *thio* (Greek for sulphur), so that we now speak of *thiosulphuric* instead of hyposulphurous acid. As a consequence of this change, sodium hyposulphite—which is a salt of thiosulphuric acid—is now properly called *sodium thiosulphate.* But the old name—and its familiar abbreviation "hypo"—still command most adherents among photographers generally.

Sodium hyposulphite is prepared on a large scale, and very cheaply, from *soda waste*, the insoluble matter which remains after the extraction of sodium carbonate from *black ash.* It is readily soluble in water, and rather deliquescent. Paper manufacturers use a great deal of "hypo" as an "anti-chlor," to remove the excess of chlorine which they use to bleach the vegetable fibres they employ; the consequence is that ordinary paper, white blotting-paper, and card-board contain a little sodium hyposulphite, and photographs mounted on such supports will be pretty sure to fade. Sodium hyposulphite in solution is best kept in a blue bottle and in a tolerably dark place. It is a good plan to keep a lump of chalk in the solution, as it neutralizes any trace of acid which may be formed. When kept in a white bottle, and exposed to sunlight, the hypo is slowly oxidized. A mixture of alum and hypo solutions rapidly decomposes, the sulphur being separated, and causing the mixture to become milky. For this reason gelatine plates that have been soaked in alum must be well washed before placing them in the "hypo," or the sulphur will be deposited in the film.

Vessels used in the photographer's laboratory to hold hyposulphite of soda should never be employed for any other purpose. They become so saturated with the fluid—which will pass right through a porcelain dish in a few days—as to contaminate every other fluid put into them.

Acids decompose "hypo," liberating free sulphur, which is deposited upon them, and is very injurious to photographic negatives or prints. For this reason the hypo solution must always be kept neutral or slightly alkaline.

SODIUM IODIDE.

Formula, NaI: Combining weight, 150.

Prepared by neutralizing hydriodic acid with sodium carbonate. From hot concentrated solutions of this salt the crystals formed are anhydrous cubes; but if the solutions are evaporated at the ordinary temperature, prismatic crystals are formed which contain two molecules of water of crystallization—$NaI+2H_2O$.

SODIUM NITRATE.

Formula, $NaNO_3$: Combining weight, 85.

Immense natural deposits of sodium nitrate occur in Chili and Peru, and hence this salt is commercially known as *Chili saltpetre.* It is purified by dissolving and re-crystallizing the natural product; but after this operation it still contains a little sodium chloride and sulphate. These may be got rid of by precipitating the nitrate from a boiling saturated solution by means of nitric acid. Sodium nitrate is deliquescent, absorbing moisture from the air. Hence it cannot be used to replace the more expensive potassium nitrate in the manufacture of gunpowder. Patents have been taken out for preventing this deliquescence by covering each particle of the sodium nitrate with a coating of paraffin; but in practice this method was not successful.

SODIUM SILICATE.

Formula, $Na_2Si_4O_9$: Combining weight, 302.

Since the molecule of this substance contains four atoms of silicon it may be called *sodium tetrasilicate*, but it is usually known as silicate of soda, or soluble glass. It can be obtained by dissolving powdered flint under pressure in hot, strong caustic soda, or by heating sand with soda-ash and charcoal. When powdered up it is readily soluble in boiling water, and forms a thick, viscid liquid. It is used in fresco painting, as a cement in the manufacture of artificial stone, and in soap making.

SODIUM SULPH-ANTIMONIATE (SCHLIPPE'S SALT).

Formula, Na_3SbS_4 : Combining weight, 318.

When 18 parts finely-powdered antimonious sulphide, 17 parts dry sodium carbonate, 13 parts slaked lime, and $3\frac{1}{4}$ parts sulphur are boiled together for some hours in a quantity of water, sodium sulph-antimoniate is formed. The liquid must then be filtered, and the filtrate evaporated, when Schlippe's salt will be obtained in beautiful crystals.

Schlippe's salt can be used to intensify negatives. It may either be applied after a solution of bichloride of mercury, or (better) after the plate has been soaked in iodide of mercury.

SODIUM SULPHITE.

Formula, $Na_2SO_3+7H_2O$: Combining weight, $126+126=252$.

Prepared by taking a saturated solution of sodium carbonate, dividing it into two parts, saturating one part with sulphurous acid, and then adding the other part. On evaporating, transparent crystals of sodium sulphite are formed. These crystals are very soluble in water, slightly soluble in alcohol.

Sodium sulphite combines eagerly with oxygen, becoming converted into sodium sulphate, Na_2SO_4. On this fact depends its use in the developer, since it takes possession of the oxygen which would otherwise go to the pyrogallic acid. It was first introduced for this purpose by Mr. Berkeley, and it is recommended to add four times as much sodium sulphite by weight as there is pyro employed. By this means a solution of pyrogallic acid can be made up and preserved for use for months, if not years, while without the Na_2SO_3 the pyro would rapidly discolor and become useless.

SODIUM TUNGSTATE.

Formula, $Na_2WO_4+2H_2O$: Combining weight, $292+36=330$.

Prepared commercially by fusing wolfram (a tungstate of iron and manganese which is a fairly common ore) with soda-ash. It crystallizes in narrow prisms, which dissolve in four parts of cold or two of boiling water. The solution is alkaline, and has a bitter taste. The crystals are insoluble in alcohol. Sodium tungstate is used to render fabrics uninflammable. In photography it has been employed to render the gold toning-bath alkaline.

STARCH.

Formula, $C_6H_{10}O_5$: Combining weight, 162.

Starch forms a large part of every plant. It occurs in the form of minute *granules*, which are insoluble in cold water, alcohol, and ether. In hot water the granules swell and burst, forming starch paste; and by continued boiling the starch may be dissolved. Iodine forms a blue compound with starch, the color disappearing with heat, but returning when the solution is cooled.

STRONTIUM CHLORIDE.

Formula, $SrCl_2+6H_2O$: Combining weight, $158\frac{1}{2}+108=266\frac{1}{2}$.

Chloride of strontium is formed when strontium carbonate (the mineral called *strontianite*) is dissolved in hydrochloric acid. It can be obtained (by crystallization) in long hexagonal needles which deliquesce in air, are very soluble in water and in alcohol. By heat the water of crystallization is driven off, and the salt remains as a white powder.

Calcium chloride is frequently present, as an impurity, but this may be removed by repeated dissolving in, and re-crystallization from hot water.

SUGAR (SUCROSE).

Formula, $C_{12}H_{22}O_{11}$: Combining weight, 342.

Cane-sugar is obtained by boiling the sweet juice of the sugar-cane until the sucrose crystallizes out. The transparent colorless crystals of sugar are soluble in one-third of their weight of water, less soluble in alcohol. When heated with silver and mercury salts, cane-sugar reduces them, and it precipitates gold from the chloride. Sugar-water dissolves lime much more rapidly than pure water. *Glucose*, or grape-sugar, is represented by the formula $C_6H_{12}O_6$. It is less sweet and less soluble than cane-sugar. It is largely present in most ripe fruits.

SULPHURIC ACID.

Formula, H_2SO_4 : Combining weight, 98.

Sulphuric acid may be considered as sulphur trioxide (SO_3 —a white crystalline solid) combined with one molecule of water. It is prepared by burning sulphur, or some ore of sulphur in air, and passing the gas thus formed (sulphur dioxide, SO_2) into a leaden chamber, where it meets with nitric peroxide and steam, and is converted into sulphuric acid. The common or commercial acid thus obtained has a slightly gray tint, and usually contains small quantities of arsenic (from the ore) and lead. The pure acid is obtained from the commercial by distillation in platinum or glass retorts.

Commercial sulphuric acid is commonly called *oil of vitriol.* It is a heavy, oily liquid (specific gravity 1.84), boiling at 640 deg. Fahr. It burns the skin, clothes, or indeed almost any organic substance upon which it falls, blackening them at the same time. This is due to the fact that it extracts *water* from these substances, leaving their carbon behind. When mixed with water the heat produced may exceed boiling-point, and for this reason the mixing should always be done in *thin* glass vessels or jugs, the acid being always *added to the water*, in small quantities at a time, and with frequent stirring.

The white precipitate which appears is sulphate of lead, which is insoluble in the dilute acid; it may be allowed to sink to the bottom, and the clear liquid then poured off. Owing to its power of absorbing water, sulphuric acid is often used for drying substances without heat; the substance and the acid being placed in separate dishes under a glass shade.

Sulphuric acid dissolves all the ordinary metals except gold and platinum. Hence it is often used for the separation of gold from silver, the latter being dissolved, and the former left behind as a dark powder.

The presence of sulphuric acid, or any soluble sulphate, in a solution, may be detected by adding a few drops of barium chloride, when a white precipitate, insoluble in nitric acid, will be formed.

SULPHUROUS ACID.

Formula, H_2SO_3: Combining weight, 82.

The true sulphurous acid is formed by dissolving sulphurous acid gas (SO_2) in water. This gas—also known as sulphurous-anhydride, and as sulphur-dioxide—is best obtained by the action of sulphuric acid on copper, aided by a gentle heat. One volume of water, at ordinary temperatures, dissolves fifty volumes of the gas. The solution turns blue-litmus red, and has a sour taste.

Sulphurous acid forms a series of salts called *sulphites*, which are easily decomposed by the stronger acids, SO_2 being liberated.

TANNIC ACID (TANNIN).

Formula, $C_{14}H_{10}O_9$: Combining weight, 322.

The nut-galls of the oak, excrescences produced by the action of insects, contain nearly half their weight of tannic acid, which is extracted by soaking the powdered galls in washed ether. From its origin it is sometimes called gallo-tannic acid. When the ether is subsequently evaporated the tannin is obtained as a yellowish amorphous substance, very soluble in water, less soluble in alcohol. It has a strongly astringent taste, and reddens blue-litmus.

With the ferric, or per-salts of iron, tannic acid gives a black precipitate, which is common writing-ink. When exposed to the air, or when treated with dilute acids, tannic acid is decomposed into gallic acid, and glucose. It yields pyrogallic acid when heated to a temperature of 400 deg. Fahr.

Gelatine and albumen are precipitated by tannin; with the former it produces a tough material, which is practically leather.

TARTARIC ACID.

Formula, $C_4H_6O_6$: Combining weight, 150.

When grape-juice is fermented—as in the manufacture of wine—it deposits an impure acid potassium tartrate, which is known as lees, tartar or argol, and from which tartaric acid is made by the addition first of chalk, then of calcium chloride, and lastly of sulphuric acid.

Tartaric acid forms large prismatic, colorless crystals, soluble in half their weight of water, and in alcohol. The aqueous solution does not keep well.

THIOSULPHURIC ACID.

Formula, $H_2S_2O_3$: Combining weight, 114.

This acid, formerly called hyposulphurous acid, is not known in the free state, but salts of it exist; the sodium salt $Na_2S_2O_3+5H_2O$ is the familiar "hypo" of the photographer.

URANIUM NITRATE.

Formula, $UO_2(NO_3)_2+6H_2O$: Combining weight, $396+108=504$.

Uranium is a rare metal, whose chief source is the ore called *pitch-blende.* By treating this ore with nitric acid uranium nitrate is obtained. On evaporation it forms fine yellow crystals which are soluble in half their weight of water, and which deliquesce by the absorption of water from the atmosphere.

VANADIUM.

Symbol V: Combining weight, 51.

Although known in its ores since 1801, vanadium was first isolated by Roscoe in 1867.

VARNISHES.

A varnish is any liquid matter which, when applied to the surface of a solid body, becomes dry, and forms a hard, glossy coating impervious to air and moisture. Varnishes generally consist of some resinous substance dissolved in a volatile liquid, which on evaporation leaves the resin in the form of a film. They are generally divided into two classes—*oil* varnishes and *spirit* varnishes—according to the substance employed as the vehicle or solvent.

For oil varnishes, either linseed oil, or oil of turpentine is employed. The drying of oil varnishes is due to oxidation.

For spirit varnishes the solvent is either alcohol (of not higher specific gravity than .815), methylated spirits, or naphtha. These dry rapidly by evaporation.

The following resins are largely used in the manufacture of varnishes. They are substances which exude spontaneously, or from incisions made in the trunks, etc., of trees. They are solid, more or less transparent, inflammable, inodorous bodies, insoluble in water, but soluble in alcohol.

Amber.—A yellowish fossil resin found chiefly on the southern shores of the Baltic Sea. It is the gum of a kind of pine tree, and is largely used in the manufacture of ornaments, mouth-pieces for pipes, etc. It is soluble in chloroform, and then forms the basis of several varnishes.

Animé, or *gum animé*, is a brownish-yellow transparent resin, the product of the locust tree of Central America.

Rosin, *resin*, or *colophony*, is the solid residue remaining in the retort after the distillation of common turpentine.

Copal, or *gum copal*, is a hard resin which exudes from certain trees that grow in the East and West Indies.

Dammar, or *gum dammar*, is mostly obtained from a coniferous tree which grows in the East Indies.

Elemi, or *gum elemi*, is a pale yellow, semi-transparent resin, brittle superficially, but soft and tough within. It is used to give toughness to lacquers and varnishes.

Lac is a resin combined with much coloring matter, which results from the puncture of the bark of certain tropical trees by an insect—*Coccus lacca*. *Stick lac* is the crude resin as broken off the trees. When melted, strained, and spread out in thin sheets it is called *shellac*. This shellac varies in color from orange to garnet; the palest being the most valuable.

Bleached lac is made by dissolving lac in a boiling solution of caustic potash, and then passing chlorine through the solution. The lac is then nearly white, and is used for pale varnishes.

Mastic.—A pale-yellowish resin found in transparent rounded beads, which soften when chewed.

Sandarac.—A resin given by two species of tropical trees (*thuja* and *juniperus*).

For photographic purposes spirit varnishes are largely employed for covering the delicate surface of the gelatine film of the negative. They are best prepared by macerating the resin in closed bottles or tins.

Mr. W. Bedford recommends the following varnish for negatives:

Button lac	½ pound
Sandarac	2 ounces
Methylated spirit	½ gallon

Shake up occasionally during a week, by which time the soluble portion will be taken up; but avoid heat, as it is better to filter off the sediment.

The common, or *brown hard spirit varnish* of the shops (when good) is made as follows:

Gum sandarac	3 pounds
Pale shellac	2 pounds
Spirits of wine	2 gallons
Dissolve, and add	
Turpentine varnish	1 quart

Agitate well, strain quickly through gauze, and after a month decant the clear portion from the sediment.

When diluted with an equal volume of methylated spirit, this makes a good varnish for negatives.

Crystal varnish is very useful for maps, prints, and articles of paper generally; but the paper must first be sized. It is made by mixing equal parts of Canada balsam and rectified oil of turpentine.

India rubber, or *flexible varnish*, is made by dissolving in the cold one and a half ounces of pure (masticated rubber), cut small, in one pint of either chloroform, ether (washed), or carbon bisulphide.

Or India rubber shavings (one ounce) may be dissolved by gentle heat in rectified mineral naphtha or benzol (one pint); but this dries badly.

The following varnishes for negatives are taken from the "British Journal Almanac":

No. 1.

Sandarac	4 ounces
Alcohol	28 ounces
Oil of lavender	3 ounces
Chloroform	5 drams

No. 2.

White, hard varnish of the shops	15 ounces
Methylated alcohol	25 ounces

This will be found to be a good and cheap varnish if durability is not required, as it is easily rubbed up for retouching upon, and easily cleaned off. Very suitable for enlarged negatives that are not to be retained.

No. 3.

Tough, hard and durable.

Shellac	1¼ ounces
Mastic	¼ ounce
Oil of turpentine	¼ ounce
Sandarac	1¼ ounces
Venice turpentine	¼ ounce
Camphor	10 grains
Alcohol	20 fluid ounces

No. 4.

Sandarac	90 ounces
Turpentine	36 ounces
Oil of lavender	10 ounces
Alcohol	500 ounces

No. 5.

This one may be rubbed down, when cold, with powdered resin, and gives a splendid surface for retouching.

Sandarac	2 ounces
Seed-lac	1 to 1½ ounces
Castor oil	3 drams
Oil of lavender	1½ drams
Alcohol	18 fluid ounces

No. 6.

Best orange shellac	1½ ounces
Methylated spirit	1 pint

Keep in a warm place until dissolved; then add a large teaspoonful of whiting or prepared chalk. Set aside to clear, and then decant. This is specially recommended for gelatine negatives.

NEGATIVE RETOUCHING VARNISH.

Sandarac	1 ounce
Castor oil	80 grains
Alcohol	6 ounces

First dissolve the sandarac in the alcohol, and then add the oil.

GROUND-GLASS OR MATT-VARNISH.

Sandarac	90 grains
Mastic	20 grains
Ether	2 ounces
Benzole	½ to 1½ ounce

The proportion of the benzole added determines the nature of the matt-surface obtained. This varnish must be applied, and allowed to dry, *without* heating the negative. For the other varnishes the glass should be gently heated both before and after they are applied.

WATER.

Formula, H_2O : Combining weight, 18.

Ice melts at 32 degs. Fahr., and the liquid water passes into water-gas (steam) at 212 degrees. When cooling, water steadily contracts until it reaches 39 degs. Fahr. (point of greatest density) and then slowly expands until it reaches 32 degs. Fahr., when it suddenly expands about one-tenth, so that ten cubic feet of water form eleven cubic feet of ice. This is the cause of the frequent bursting of water-pipes in frosty weather.

Pure water is a compound of the two gases, oxygen and hydrogen, but ordinary water is far from pure. Indeed, it is doubtful if perfectly pure water has ever been obtained. Ordinary water contains impurities of two kinds: (*a*) matter *suspended* in the water, as sand, mud, etc.; and (*b*) matter *dissolved* in the water, as salts of lime, etc. From matters in suspension the water can be freed by filtration; while the dissolved substances are left behind when the water is distilled and re-distilled.

Ordinary spring water is more or less *hard* from the presence of salts of lime—usually the carbonate of lime. Rain-water is fairly pure in the country, but in towns, where it falls through dirty air and over dirty roofs, it is always much contaminated with soot, etc. When the rain-water runs over or through the rocks it dissolves some of the materials of which they are composed, and these cause it to be *hard.*

All rain-water contains carbonic acid gas dissolved out of the air, and it is to the presence of this acid that rain-water owes its power to dissolve limestone rocks. When the hard water is boiled, the carbonic acid gas is driven off, and the carbonate of lime is then deposited on the bottom and sides of the vessel. Such a deposit, called fur, may be seen inside most kettles. Other common impurities in spring or river-water are sulphates of lime and of magnesia, and as these cannot be removed by boiling, they make the water *permanently hard.*

The water of shallow wells and of rivers near large towns usually contains some suspended *organic* matter, derived chiefly from sewage, which may be a cause of great danger to those who drink it.

For many purposes in photography ordinary tap water is sufficiently pure, as for washing the plates after development, washing prints, etc.; but for making most solutions and for mixing the developing solution *distilled* water is far better.

To distill water we require a *still*, or vessel in which to boil the water; a *worm*, in which to cool the steam; and a receiver into which the condensed water may pass. These articles are frequently made of tin, or better, of copper.

ZINC BROMIDE.

Formula, $ZnBr_2$: Combining weight, 225.

Prepared by passing bromine vapor over red-hot zinc. It is a white, crystalline salt which greedily absorbs moisture, and so deliquesces when exposed to the air.

ZINC CHLORIDE.

Formula, $ZnCl_2$: Combining weight, 136.

Prepared by dissolving zinc in hydrochloric acid. It is a white and very deliquescent substance, very soluble in water and in alcohol. From its great affinity for water it is sometimes employed for removing the elements of that liquid from organic compounds.

Zinc Iodide.

Formula, ZnI_2: Combining weight, 329.

When zinc filings are heated with iodine, they combine to form iodide of zinc, a colorless, deliquescent, unstable substance.

All these salts of zinc have an acid reaction, turning blue litmus red. They cause vomiting, which is fortunate, as they are strong poisons.

Zinc Hypochlorite.

Formula, $ZnCl_2O_2$: Combining weight, 168.

This salt of hypochlorous acid may be prepared by adding a solution of zinc sulphate to a solution of calcium hypochlorite, and then filtering off the insoluble calcium sulphate formed. In this state it will be mixed with zinc chloride, but this latter substance will not interfere with its use as a hypo eliminator. Its use in photography depends upon the fact that a solution of hypochlorite of zinc will decompose hyposulphite of soda, so that it is used to eliminate the hypo from prints after fixing. When a neutral solution of hypochlorite of zinc is added in excess to a solution of hyposulphite of soda, a mutual reaction takes place between the two, sodium hydrogen sulphate and zinc chloride being formed. There is a certain amount of danger in its use, as it is an unstable body and gives off chlorine on keeping. If this chlorine comes into contact with hyposulphite of soda, free hydrochloric acid is evolved, and hydrochloric acid in contact with hyposulphite of soda acts upon it with deposition of free sulphur, which will be deposited in the pores of the paper, and will probably combine with the silver.

Zirconia (Zirconium Oxide).

Formula, ZrO_2: Combining weight, 122.

Zirconia is a hard, white powder, resembling silica. Compressed into cylinders, it has been recommended for use in the "lime-light" instead of lime. It is, however, extremely difficult to obtain pure zirconia. It is a non-conductor of heat, so that before the mixed gases it gives a bright white spot of light not more than a quarter of an inch in diameter.

TABLE OF THE PRINCIPAL SUBSTANCES WHICH ARE KNOWN TO BE ACTED UPON BY LIGHT.

SUBSTANCE.	FIRST OBSERVER.	DATE.
SILVER.		
Nitrate solution, mixed with chalk, gives in sunshine copies of writing	J. H. Schulze	1727
Nitrate solution on paper	Hellot	1737
Nitrate photographically used	Wedgwood & Davy	1802
Nitrate on silk	Fulhame Rumford	1797 1798
Nitrate with white of egg	B. Fischer	1812
Nitrate with lead salts	Herschel	1839
Chloride	J. B. Beccarius	1757
Chloride in the spectrum	Scheele	1777
Chloride photographically used	Wedgwood	1802
Chloride blackened	Lassaigne	1839
Iodide	Davy	1814
Iodide by action of iodine (on metallic silver)	Daguerre	1839
Iodide photographically used	Herschel	1840
Iodide with gallic acid	Talbot	1841
Iodide with ferrous sulphate	Hunt	1844
Chloride and iodide by chlorine and iodine (on metallic silver)	Claudet	1840
Bromide	Balard	1826
Bromide by action of bromine (on metallic silver)	Goddard	1840
Sulpho-cyanide	Grotthus	1818
Nitrite	Hess	1828
Oxide with ammonia	Mitscherlich	1827
Sulphate	Bergmann	1779
Chromate	Vauquelin	1798
Carbonate	Buchholz	1800
Oxalate	Bergmann	1779
Benzoate	Trommsdorf	1793
Citrate	Vauquelin	1798
Kinate	Henry and Plisson	1829
Borate	Rose	1830
Pyro-phosphate	Stromeyer	1830
Lactate	Pelouze and Gay-Lussac	1833
Formiates	Hunt	1844
Fulminates	Hunt	1844
Sulphide by vapor of sulphur (on metallic silver)	Niepce	1820
Phosphide by vapor of phosphorus (on metallic silver)	Niepce	1820

Table of the Principal Substances, etc.—*Continued*

Substance.	First Observer.	Date.
Gold.		
Oxide	Scheele	1777
Chloride on paper	Hellot	1737
Chloride on silk	Fulhame	1794
Chloride in etherial solution	Rumford	1793
Chloride with ferro-cyanide and ferri-cyanide of potassium	Hunt	1844
Chloride and oxalic acid	Döbereiner	1831
Chromate	Hunt	1844
Plate of gold and iodine vapor	Goddard	1842
Platinum.		
Chloride in ether	Gehlen	1804
Chloride with lime	Herschel	1840
Iodide	Herschel	1840
Bromide	Hunt	1844
Cyanide	Hunt	1844
Double chloride of platinum and potassium	Döbereiner	1828
Mercury.		
Oxide (mercurous)	Gay-Lussac and Thénard	1811
Oxide	Davy	1812
Oxide (mercuric)	Davy	1797
Oxide (more accurate observations)	Abildgaard, Harrup not till	1797 1801
Chloride (mercurous)	R. Neumann, previous to	1739
Chloride (mercuric)	Boullay	1803
Chloric with oxalic acid	Bergmann	1776
Sulphate	Meyer	1764
Oxalate (mercuric)	Bergmann	1776
Oxalate (mercurous)	Harff	1836
Sulphate and ammonia (mercurous)	Fourcroy	1791
Acetate (mercurous)	Garot	1826
Bromide (mercuric)	Löwig	1828
Iodide (mercurous)	Torosewicz Artus	1836 1836
Iodide (mercuric)	Field	1836
Citrate (mercuric)	Harff	1836
Tartrate and Potassium (mercurous)	Carbonell & Bravo.	1831
Carbonate (mercuric)	Davy	1812
Nitrate	Herschel	1840
Sulphite (mercuric)	Vitruvius	1, B.C.
Iron.		
Sulphate (ferrous)	Chastaing	1877
Chloride (ferric) and alcohol	Bestuscheff	1725
Chloride and ether	Klaproth	1782
Oxalate (ferric)	Döbereiner	1831
Ferro-cyanide of potassium	Heinrich	1808
Sulpho-cyanide	Grotthus	1818
Prussian blue	Scopoli	1783
Ferric Citrate with ammonium	Herschel	1840
Ferric Tartrate	Herschel	1840
Chromate	Hunt	1844

Table of the Principal Substances, etc.—*Continued.*

Substance.	First Observer.	Date.
Copper.		
Chloride (cupric dissolved in ether)	Gehlen	1804
Oxalate with sodium	A. Vogel	1813
Chromate	Hunt	1844
Chromate with ammonium		
Carbonate		
Iodide		
Sulphate		
Chloride (cuprous)	A. Vogel	1859
Copper plates (iodized)	Kratoch Talbot	1841 1841
Manganese.		
Sulphate	Brandenburg	1815
Oxalate	Suckow	1832
Potassium permanganate	Frommberg	1824
Peroxide and cyanide of potassium	Hunt	1844
Chloride	Hunt	1844
Lead.		
Oxide	Davy	1802
Iodide and sulphite	Schönbein	1850
Peroxide	Gay-Lussac	1811
Red lead and cyanide of potassium	Hunt	1844
Acetate	Hunt	1844
Nickel.		
Nitrate	Hunt	1844
Nitrate with ferro-prussiates		
Iodide		
Tin.		
Purple of Cassius	Uncertain	....
Various Substances.		
Cobalt	Hunt	1844
Arsenic sulphide (realgar)	Sage	1803
Antimony sulphide	Suckow	1832
Bismuth salts	Hunt	1844
Cadmium salts		
Rhodium salts		
Vanadic salts	Roscoe	1874
Iridium ammonium-chloride	Döbereiner	1831
Potassium bichromate	Mungo Ponton	1838
Potassium with iodide of starch	Becquerel	1840
Metallic chromates	Hunt	1843
Chlorine and hydrogen	Gay-Lussac and Thénard	1809
Chlorine (tithonized)	Draper	1842
Chlorine and ether	Cahours	1810
Chlorine in water	Berthollet	1785
Chlorine and ethylene	Gay-Lussac and Thénard	1809
Chlorine and carbon monoxide	Davy	1812
Chlorine and marsh-gas	Henry	1821
Chloride and hydrocyanic acid	Serullas	1827

TABLE OF THE PRINCIPAL SUBSTANCES, ETC.—*Continued.*

SUBSTANCE.	FIRST OBSERVER.	DATE.
VARIOUS SUBSTANCES.		
Bromide and hydrogen	Balard	1832
Iodine and ethylene	Faraday	1821
Cyanogen, solution of	Pelouze and Richardson	1837
Various other methyl compounds	Cahours	1848
Hydrocyanic acid	Torosewicz	1836
Hypochlorites (calcium and potassium)	Döbereiner	1813
Uranium chloride and ether	Gehlen	1804
Molybdenate of potassium and tin salts	Jager	1800
Crystallization of salts under influence of light	Petit Chaptal Dize	1722 1788 1789
Phosphorus (in hydrogen, nitrogen, etc)	Bockmann	1800
Phosphoretted hydrogen	A. Vogel	1812
Nitric acid	Scheele	1777
Hog's fat	Vogel	1806
Palm oil	Fier	1832
Asphalt	Niepce	1814
Resins (mastic, sandarac, gamboge, ammoniacum, etc)	Senebier	1782
Guaiacum	Hagemann	1782
Bitumens all decomposed, all residues of essential oils	Daguerre	1839
Colored extracts from flowers	Senebier	1782
Similar coloring matters spread on paper	Herschel	1842
Yellow wax, bleached	Pliny	1st cent'y, A.D.
Eudoxia macrembolitissa (purple dye)		10th cent'y.
Other purple dyes	Cole Réaumur	1684 1711
Oils generally	Senebier	1782
Nitric ether	Senebier	1782
Nicotine	Henry and Bouton-Charlard	1836
Santonine	Merk	1883

CHAPTER XIV.

CHEMICAL COMPOSITION OF THE SENSITIVE SURFACES EMPLOYED TO RETAIN THE CAMERA-IMAGE IN PHOTOGRAPHY, AND THE CHEMISTRY OF THEIR PREPARATION.

The first man who obtained an image upon a sensitive surface by the means of a lens, was Humphrey Davy, the famous chemist, in or shortly before the year 1802.* He used paper coated with silver chloride, and his lenses were those of the solar microscope. But silver chloride is much less sensitive to light than certain other salts of silver; and for use in the camera it has been displaced first by silver iodide, and then by silver bromide.

Henry Fox Talbot, too, used silver chloride in his "Process of Photogenic Drawing" which he published in 1839. He made an advance upon Davy's work, in that he discovered that the presence of silver nitrate (upon the coated paper, and intimately associated with the silver chloride) greatly increased the sensitiveness to light of the latter substance. He formed the silver chloride in and upon the paper, by soaking the paper in a weak solution of common salt, and then brushing it over *twice* with a solution of silver nitrate, of strength about sixty grains to the ounce. By the mixture and chemical combination of these two materials, silver chloride was formed as follows:

$NaCl$	+	$AgNO_3$	=	$AgCl$	+	$NaNO_3$
Sodium	*and*	Silver	*produce*	Silver	*and*	Sodium
Chloride		Nitrate		Chloride		Nitrate.

The slight excess of silver nitrate (due to the second brushing), acts as a *sensitizer*, absorbing and combining with the chlorine gas which is given off when the prepared paper is exposed to the action of light.

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* See "Journal of the Royal Institution," London; Vol. I.

$2AgNO_3$	+	Cl_2	+	H_2O	=	$2AgCl$	+	$2HNO_3$	+	O
Silver Nitrate	*and*	Chlorine	*and*	Water	*produce*	Silver Chloride	*and*	Nitric Acid	*and*	Oxygen.

But although Talbot succeeded in obtaining images in the camera, by means of paper coated in this way, yet the necessary exposure was very long—from thirty minutes to one hour—and its use for this purpose was soon discontinued. It is to be noticed that with it Talbot obtained a *printed-out* negative image in the camera; no subsequent process of development being necessary, or indeed possible. This sensitive surface of silver chloride has formed, however, the principal printing process for obtaining positive prints from negatives secured by other methods, from Talbot's time down to the present day. It is, in fact, the substance with which ordinary "silver" or "sensitized" paper is coated. The properties of silver chloride are described more fully in the Chapter on "The Chemistry of Printing."

Niepceotype, or Heliography.—The first *permanent* pictures secured by the agency of light, were those obtained by Joseph Nicephore Niepce, of Chalons, about the year 1816. He dissolved bitumen in oil of lavender, and coated metal plates with it. The plates were then exposed in a camera for several hours. The effect of light was to render the bitumen upon which it acted *insoluble* in oil of lavender; so that the picture could be developed by subsequent washing with that liquid. In repeating this experiment, we find that petroleum acts as well as the more expensive lavender oil.

Bitumen, or asphaltum, is composed of the elements hydrogen and carbon, and is therefore termed a hydrocarbon. By exposure to light these elements combine with the oxygen present in the air, or with the moisture in the air touching the plate. The "oxidized hydrocarbon" is then insoluble in liquids in which the hydrocarbon alone would readily dissolve. The change is too complex, and too little of its exact nature is certainly known to enable us to represent it by a chemical equation.

Those who wish to repeat Niepce's experiment will find it better to expose the plate coated with asphalt beneath a negative, rather than in the camera; the necessary exposure to light will then only be ten or fifteen minutes.

Preparation of the Sensitive Surface for the Daguerreotype Process.—In the process published by Daguerre in 1839, he obtained a surface extremely sensitive to light by exposing the surface of a silver plate (silver plated upon copper was always used, to save expense) to the action of the vapor of iodine. Iodide of silver was, of course, produced by the combination of the two elements:

$$\begin{array}{ccccc} \mathrm{Ag} & + & \mathrm{I} & = & \mathrm{AgI} \\ \text{Silver} & \textit{and} & \text{Iodine} & \textit{produce} & \text{Silver-Iodide.} \end{array}$$

The iodine was placed at the bottom of a box, and the plate of silver was suspended over it. Iodine readily evaporates, and in two or three minutes the surface of the silver plate (as seen through a little window in the box) had lost its metallic lustre, and acquired the fine yellow hue of iodide of silver. The metallic silver *behind* the surface layer of silver iodide acted as a sensitizer, absorbing the iodine which was given off under the influence of light.

But this surface of pure silver iodide required a rather long exposure in the camera—from fifteen to twenty minutes; and it was not until J. F. Goddard discovered, in 1840, that by exposing the iodized silver plate to the fumes of the liquid non-metallic element bromine the necessary exposure could be reduced from minutes to seconds, that the daguerreotype process became a real success. The bromine united with the silver iodide to form a compound which may be called bromo-iodide of silver, and which was extremely sensitive to light. The change was indicated by the yellow surface of the plate assuming a rosy hue.

It is true that Fox Talbot had, in 1839, discovered the great sensitiveness to light of silver bromide. But its application to the daguerreotype process, and its practical success as a diminisher of exposure are due to Goddard.

How Talbot Prepared his Calotype Paper.—It is probable that Fox Talbot availed himself of ideas suggested both by Daguerre and by an English clergyman named J. B. Reade, in the working out of the process which he patented in 1841 under the name of "Calotype;" but this in no way detracts from the credit due to him for devising so practical and successful a method. He substituted silver iodide for the silver chloride which he had previously employed; and he gave only a short exposure in the camera, developing the latent image thus impressed by a method which Reade had not indeed published, but which he had made known to some of his friends, including Andrew Ross, the famous optician.

By the calotype process, Talbot brushed a solution of silver nitrate over paper, which was then dried and dipped into a solution of potassium iodide. The strength of the solutions was so arranged that there should be an excess of the iodide. By the combination of these two chemicals the paper was covered with a yellow coating of silver iodide:

$AgNO_3$	+	KI	=	AgI	+	KNO_3
Silver Nitrate	*and*	Potassium Iodide	*produce*	Silver Iodide	*and*	Potassium Nitrate.

In this state the paper was not sensitive to light, for there was no sensitizer present to combine with the iodine which light would liberate.

When the iodized paper was required for use, it was brushed over with a mixture of gallic acid, acetic acid, and nitrate of silver. It might then be exposed while wet, or it could be dried and kept for use. The "gallo-nitrate of silver," as the mixture just described was called, acted both as a sensitizer and as a developer; the silver nitrate fulfilling the former function, while the gallic acid *developed* the picture. The acetic acid played the part of a restrainer.

The calotype process was much practised—principally by amateurs, and for landscape work—from 1841 to 1855, or thereabouts.

Chemistry of the Albumen Process of Niepce de St. Victor.—In 1847, the younger Niepce substituted glass plates for the paper support used by Talbot in his calotype process. To enable the chemicals employed to adhere to the glass, Niepce used albumen (white of egg), in which he dissolved potassium iodide, potassium bromide, and sodium chloride (common salt). He then converted these three substances into the corresponding salts of silver by immersing the coated glass in a bath of silver nitrate.

$AgNO_3$	$+$	KI	$=$	AgI	$+$	KNO_3
Silver Nitrate	*and*	Potassium Bromide	*produce*	Silver Iodide	*and*	Potassium Nitrate.
$AgNO_3$	$+$	KBr	$=$	$AgBr$	$+$	KNO_3
Silver Nitrate	*and*	Potassium Bromide	*produce*	Silver Bromide	*and*	Potassium Nitrate.
$AgNO_3$	$+$	$NaCl$	$=$	$AgCl$	$+$	$NaNO_3$
Silver Nitrate	*and*	Sodium Chloride	*produce*	Silver Chloride	*and*	Sodium Nitrate.

The plates were then ready for exposure (wet or dry), and were afterwards developed with a solution of gallic acid. This albumen process gave beautiful results, but it was very slow; the usual length of exposure being from ten to twenty minutes.

Chemistry of the Preparation of Wet Collodion Plates.—The wet collodion process was the work of F. S. Archer, in 1851. It is most interesting to trace the evolution of photographic processes; and nothing can be clearer than the fact that the collodion process (which reigned supreme from 1851 to 1879) was the outcome of the calotype and the albumen processes. Archer substituted collodion for albumen as a means of causing the chemicals to adhere to the glass. He first coated the glass plate with collodion in which potassium iodide and bromide had been dissolved. The coated plate was then dipped into a solution of silver nitrate, when what chemists call "double decomposition" took place, and silver iodide and bromide were formed within and upon the collodion. A certain amount of the silver nitrate solution also clung to the surface of the plate, and acted as a sensitizer. We may represent the action of the silver nitrate as a sensitizer by an equation:

$2AgNO_3$	$+$	I_2	$+$	H_2O	$=$	$2AgI$	$+$	$2HNO_3$	$+$	O
Silver Nitrate	*and*	Iodine	*and*	Water	*produce*	Silver Iodide	*and*	Nitric Acid	*and*	Oxygen.

The other equations are the same as those just given for the albumen process. The plate was exposed, while still wet, in the camera; and was afterwards developed by pouring upon it a mixture of pyrogallic acid and acetic acid.

With more experience in the working of the wet collodion process, it was found that the best halogens with which to "salt" or impregnate the collodion were ammonium iodide and cadmium bromide. The chemical changes produced when collodion so salted is dipped into a bath of silver nitrate solution may be expressed by the following two equations:

$AgNO_3$	$+$	NH_4I	$=$	AgI	$+$	NH_4NO_3
Silver Nitrate	*and*	Ammonium Iodide	*produce*	Silver Iodide	*and*	Ammonium Nitrate.
$2AgNO_3$	$+$	$CdBr_2$	$=$	$2AgBr$	$+$	$Cd(NO_3)_2$
Silver Nitrate	*and*	Cadmium Bromide	*produce*	Silver Bromide	*and*	Cadmium Nitrate.

The inconvenience of carrying a portable dark-room, and a large glass vessel ("bath") to hold the nitrate of silver solution, together with all the other articles necessary to sensitize and to develop a wet collodion plate, was very great. For the plate had to be exposed while *wet*. If the silver nitrate solution were washed off and the plate dried, it was found to have lost much or all of its sensitiveness to light. If the plate were dried with the nitrate solution still upon it, the silver nitrate crystallized out, forming a network of crystals which spoilt the even surface of the collodion. This drying-up of the film prevented very long exposures being given in the camera, such as were frequently necessary for interiors, etc. Moreover, it was necessary, after exposure, to develop the plate before it had time to dry. For these reasons the photographer was compelled to drag a dark-tent and all the necessary materials for sensitizing and developing his plates, about with him. Well may the modern kodakist shudder as he reads of those times!

Dry Collodion Plates.—Very soon after Archer's publication of the wet collodion process in 1851, attempts were made to reduce, or do away with, the necessity for exposing and developing the plate while still wet. The first attempts took the form of preventing evaporation, as when M. Girod applied a plate of glass in contact with the wet film, in 1853; but it is evident that this would be likely to abrade and injure the delicate skin of collodion. Then Messrs. Crookes and Spiller, in 1854, coated the wet collodion with a solution of nitrate of zinc. This substance absorbs moisture from the air, and so keeps the film from drying up. Then Shadbolt and Lyte, in the same year, coated the collodion film with a solution of grape sugar, or of honey; which again kept the surface moist. Oxymel—a mixture of vinegar and honey—was recommended for the same purpose by J. D. Llewelyn, in 1856. But in practice all these methods were found to be but very poor makeshifts. In 1857 a Mr. H. N. King managed to keep the surface of his plates moist without doubt, for he carried his plates in a light-tight box filled with distilled water!

Another great trouble to the early experimenters who attempted to obtain "dry" collodion plates, was the fact that the collodion film when dry had a great tendency to flake or scale off from the glass plate. This was obviated in 1859 by the introduction by Hardwich, Barnes, and others, of various materials, such as gelatine, albumen, India-rubber, etc., with which the glass plate was thinly coated *before* it was covered with collodion. Any such adhesive was called a "substratum," and the collodion adhered firmly to it.

Successful Collodion Dry Plates.—The first succesful dry-plate process with collodion was the discovery of Dr. J. M. Taupenot, in 1855. He washed the sensitized collodion plate, and then flowed it over with iodized albumen; the plate was then again sensitized and again washed; finally it was dried. This process was followed by many others; and many substances, such as gelatine, gallic acid, gum arabic, tannin, coffee, tea, etc., were used to flow over the previously sensitized and washed collodion plates. Such substances received the name of "preservatives," because they acted as a kind of varnish, preserving the surface of the film from the injurious action of the air; but they also acted as sensitizers, absorbing the halogen which was given off under the action of light. Further, by filling up the pores of the collodion they offered an easy way of access to the film when the developer was subsequently applied. Perhaps the most successful of the numerous preservatives was *tannin*, which was recommended by the late Major Russell in 1861–65.

Emulsion Photography.

An "emulsion" is the name applied to a liquid which contains innumerable particles of some solid substance, the particles being so small and so nearly of the same specific gravity as the liquid, that they remain suspended in the latter for a longer or a shorter period of time. Thus milk is an emulsion. It consists of countless particles of fat (cream) suspended in a watery fluid.

As early as 1853 the French worker, Gaudin, sought to prepare a sensitive collodion or *photogene*, which could be simply poured on to plates or paper, and then dried. The cause of his failure—and that of some later experimenters—consisted in the use of *iodide* of silver. When this substance is shaken up in collodion, its particles clot together and subside to the bottom. This difficulty was overcome in 1864 by B. J. Sayce and W. B. Bolton. They formed silver *bromide* in the collodion, and found that they had got a good "emulsion." For the particles of silver bromide remain suspended in the gelatine very much as the fat-globules remain suspended in milk.

Chemistry of Collodion Emulsion-Making.—To make a satisfactory collodion emulsion for negative work, it is necessary to first dissolve a soluble bromide in alcohol and add it to some collodion. Silver nitrate is also dissolved in alcohol and added gradually to the bromized collodion, which must be kept well agitated. Supposing zinc bromide to have been employed, the following chemical reaction then takes place:

$$\underset{\substack{\text{Silver}\\\text{Nitrate}}}{2AgNO_3} \quad \underset{\textit{and}}{+} \quad \underset{\substack{\text{Zinc}\\\text{Bromide}}}{ZnBr_2} \quad \underset{\textit{produce}}{=} \quad \underset{\substack{\text{Silver}\\\text{Bromide}}}{2AgBr} \quad \underset{\textit{and}}{+} \quad \underset{\substack{\text{Zinc}\\\text{Nitrate.}}}{Zn(NO_3)_2}$$

This equation would show that the silver nitrate and the zinc bromide should be mixed together in the proportion of 340 parts by weight of the former to 225 parts of the latter.

In practice, however, a slight excess of the silver nitrate is always employed.

The zinc nitrate which is formed must be removed from the emulsion; and this is done by washing the emulsion well with water, either before coating the plates, or after. It is found to be impossible to wash away *all* the excess of silver nitrate. Some silver nitrate always remains clinging to the molecules of silver bromide, and this *acts as a sensitizer.* Carey Lea showed, in 1870, that it was useful to add a few drops of nitric acid to the emulsion, in order to prevent fog. It was usual to flow over the coated and washed plate a solution of tannin. This did not increase the sensitiveness, but it was useful in the other ways we have pointed out.

"Ripening" of Collodion Emulsion.—After the ingredients of a collodion emulsion had been well shaken up together, it was found to be a good plan to leave the emulsion for twenty-four hours to "ripen," as it was called. This ripening consists in an aggregation of the molecules of silver bromide, so as to form particles of the size most sensitive to light.

The collodion emulsion dry-plate process was much used for landscape work, and by travellers, between 1870 and 1880. It was slow—much slower on the average than wet collodion—but good work was done with it.

Chemistry of Gelatine Emulsion-Making.—Several early workers attempted to use gelatine, instead of collodion, in the preparation of a surface sensitive to light. The first success in this direction was due to Dr. R. L. Maddox, in 1871; he, however, had not time to work out the process so that it should be a commercial success. Burgess, in 1873, and Kenneth during the years 1876–77, tried hard to introduce gelatine emulsion dry-plates to the English market; but without success. Then came the discoveries of Bennett (1878) and of Mansfield (1879), showing that extraordinary sensitiveness was conferred upon a gelatine emulsion when it was carefully *heated.* The increase in rapidity "did the trick"; and gelatine displaced collodion in 1879–80.

The following short outline of the method by which several millions of gelatine dry-plates are now prepared annually will enable us to explain the chemical and physical changes which take place during this manufacture:

A. In 8 ounces of distilled water soak 40 grains of gelatine; add 180 grains of ammonium bromide and 10 grains of potassium iodide. Heat gently till all is dissolved.

B. In 1 ounce of distilled water dissolve 100 grains of silver nitrate; to this add strong ammonia, drop by drop, till the precipitate at first formed just disappears.

C. In the dark-room, warm the solution *A* to 170 deg. F.; and add to it, by degrees, 165 grains of silver nitrate. When this has dissolved, add solution *B.* Shake well, and stew for two hours at a temperature of 170 deg. F.

D. Cool the emulsion down to 80 deg. F., and add 300 grains of hard gelatine. Heat the whole to 100 deg. F., and mix well. Now place the vessel containing the emulsion in cold water, when it will quickly "set" to a stiff jelly.

E. *Wash* the emulsion well, by squeezing it through coarse canvas into several changes of water.

F. Add 1 ounce of alcohol to the emulsion; dissolve it by gentle heat; make the total quantity up to 10 ounces by adding distilled water. Lastly, filter the emulsion by squeezing it through swansdown calico, and it is ready for coating the plates. Such an emulsion will possess extremely high sensitiveness to light.

The only certain chemical reactions which take place in making a gelatine emulsion are those between the silver nitrate and the soluble bromide and iodide employed.

$AgNO_3$	+	NH_4Br	=	$AgBr$	+	NH_4NO_3
Silver Nitrate	*and*	Ammonium Bromide	*produce*	Silver Bromide	*and*	Ammonium Nitrate.
$AgNO_3$	+	KI	=	AgI	+	KNO_3
Silver Nitrate	*and*	Potassium Iodide	*produce*	Silver Iodide	*and*	Potassium Nitrate.

Sometimes the potassium iodide is omitted; but its use is generally considered to give additional clearness to the plates.

The object of *washing* the emulsion is to get rid of the extraneous salts—the nitrates of ammonium and potassium.

By heating the emulsion, and also by the addition of *am-*

monia, we cause the molecules of silver bromide to aggregate together until they form particles averaging the eight-thousandth part of an inch in diameter. It is when they are of this size that silver bromide particles are most sensitive to light.

The proof that silver bromide could exist in several distinct molecular forms, each differing in sensitiveness to light, was first published by the Belgian chemist, Stas, in 1874. Ten years later, M. de Pitteurs studied the same subject, specially from a photographic point of view; and the results of his investigations are shown in the following table:

TABLE SHOWING THE EIGHT MODIFICATIONS, OR ALLOTROPIC FORMS, OF SILVER BROMIDE.

By Transmitted Light.		By Reflected Light.	Occurrence.
Semi-transparent.	Orange.	Slate-blue.	In fresh collodion emulsion.
		Bluish-white.	Older bromide of silver in collodion wet plates.
	Reddish-orange.	Bluish-white.	In very sensitive wet collodion plates.
		Yellowish-white.	In very old bromide of silver in collodion.
Almost opaque.	Violet-blue.	Yellowish-white.	In very sensitive collodion emulsion.
		Greenish-yellow.	Bromide of silver in gelatine; sensitiveness medium.
		Green or violet-green.	Very sensitive gelatine emulsion.
	Blue.	Indistinct.	Slightly sensitive silver bromide in collodion, yielding indistinct pictures. Affected by red end of spectrum.

It is either the sixth or the seventh of these forms of silver bromide which the modern plate-maker aims at securing for his sensitive dry-plates ; and he is guided to some extent during the preparation of the emulsion by the color of a drop of the liquid emulsion when placed on a glass plate. The *cause* of the growth in size of the molecules of silver bromide—and of the consequent greater sensitiveness to light—is the fact that part of the silver bromide is dissolved by the hot liquid in which it is formed, and by the ammonia which is present. This dissolved silver is afterwards deposited upon the undissolved particles, causing them to increase in size from their original diameter (which is about the one twenty-thousandth part of an inch) to the one eight-thousandth part of an inch. The extremely small particles transmit ruby light; the larger ones transmit blue light.

It is not at all a difficult task to prepare a good gelatine emulsion. To the amateur plate-maker the difficulties lie rather in the subsequent work of coating glass plates evenly with the said emulsion, and then drying these plates in a perfectly dark room, free from dust, and at a certain rate.

Gelatine as a Sensitizer.—In our modern gelatine dry-plates it is found to be quite unnecessary (harmful, in fact) to have any excess of nitrate of silver present to act as a sensitizer; neither is it requisite to coat the plates with tannin, or with any other preservative. The fact is that gelatine is itself able to act as a "sensitizer," and to combine with the small quantities of bromine and of iodine which are given off when sunlight acts upon such a plate. This is the cause of the great superiority in sensitiveness of gelatine dry-plates over collodion or albumen. The gelatine is (comparatively) a powerful sensitizer. The German chemist, Knop, found [*] that gelatine could combine with nearly one-third its weight of bromine, forming a yellowish insoluble bromo-gelatine.

Celluloid as a Support for Gelatine Emulsion.—In 1856 a Birmingham chemist named Parkes succeeded in converting a variety of gun-cotton into a horny substance which was named "celluloid." In 1888 certain American manufacturers prepared a *transparent* kind of celluloid, and this is now largely used by professional plate-makers in lieu of glass as a support for the gelatine emulsion. The Eastman Company use celluloid which is only the four-hundredth part of an inch in thickness. This thin celluloid is quite flexible, and after coating, it is wound into rolls, which are used with a special piece of apparatus called a "roll-holder," which is fitted to the back of the camera. Other makers use a stouter kind of celluloid, which lies in the dark-slide just like a sheet of glass. The advantages of celluloid over glass are, of course, its greater lightness and non-liability to breakage.

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[*] *Chem. Centralblatt, 1879.*

CHAPTER XV.

THE CHEMICAL ACTION OF LIGHT—NATURE OF THE LATENT IMAGE.

The action of light upon the salts of silver is perhaps the most difficult and vexed question in the chemistry of photography. Exposure to sunlight for even the ten-thousandth part cf a second produces a change in the bromide of silver with which our dry-plates are coated. With short exposures like this, no *visible* change is produced; but by the action of certain chemicals, the invisible, latent, or photographic image can be *developed*, and made visible as a dark-colored substance. But a visible image, indistinguishable from either the latent or the developed image by all the tests which we are able to apply, is obtained—is "printed out," as we say—when the plate is exposed for a much longer time (half an hour, or more) to the action of light. It has happened to us more than once, that, after a very long exposure, a portion of the image (a window for example) has been visible as a dark patch when the plate has been removed from the dark-slide.

The question which we have now to consider is, what is the chemical composition (1) of the latent image, (2) of the developed image, and (3) of the printed-out image?

It may be assumed—though it has not been absolutely proved—that these three images are of the same nature, and the same chemical composition. Eight or ten theories have been advanced, and we shall proceed to give some account of each.

The substances which we shall consider principally, as those most easily affected by light, will be the chloride, the iodide, and the bromide of silver. And it may be taken as fairly certain that the action of light upon silver iodide, upon silver bromide and upon silver chloride, will be similar in nature and in effects. These three salts of silver are called the *silver haloids*, or the haloid salts of silver. Silver fluoride (AgF) is also a silver haloid; but as it is not used in photography we need not notice it here.

The Effect of Light upon the Silver Haloids to produce Metallic Silver:—Scheele and Guthrie's Theory.—The first man to study the chemical effect of light upon any silver salt was Charles William Scheele, a Swedish chemist, in the year 1777. He writes: *

"I mixed as much of distilled water with well-edulcorated horn-silver as would just cover this powder. The half of this mixture I poured into a white crystal phial, exposed it to the beams of the sun, and shook it several times each day; the other half I set by in a dark place. After having exposed the one mixture during the space of two weeks, I filtered the water standing over the *luna cornua*, grown already black; I let some of this water fall by drops in a solution of silver, which was immediately precipitated into horn-silver.

"I precipitated a solution of silver by sal-ammoniac; then I edulcorated and dried the precipitate, and exposed it to the beams of the sun for the space of two weeks, when the surface of the white powder grew black, after which I stirred the powder, and repeated the same several times. Hereupon I poured some caustic spirit of sal-ammoniac on this, in all appearance, black powder, and set it by for digestion. This menstruum dissolved a quantity of *luna cornua*, though some black powder remained undissolved. The powder having been washed was for the greater part dissolved by a pure acid of nitre, which by the operation acquired volatility. This solution I precipitated again by means of sal-ammoniac into horn-silver. Hence it follows that the blackness which the *luna cornua* acquires from the sun's light is silver by reduction."

Converting Scheele's terms into those of the present day, we can express the results which he believed he obtained by exposing silver chloride (horn-silver or *luna cornua* to the light by the following equation:

$AgCl$	+	Ag	+	Cl
Silver Chlorine	*produces*	Metallic Silver	*and*	Chlorine.

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* "Traité de l'Air et du Feu."

The selection of silver *chloride* by Scheele for this experiment will easily be understood, if we remember that neither silver *bromide* nor silver *iodide* was discovered till many years after. What the great Swede did was to select the most sensitive substance to light known to that age, and to endeavor to find out what change—if any—was produced by light in its chemical composition. His idea of exposing the silver chloride to light while in distilled water was decidedly neat. He reasoned that if any substance were given off or detached from the chloride by the action of light, that substance would be arrested by and become dissolved in the water. His theory proved correct. When he poured off the clear water and added it drop by drop to a "solution of silver" (*i.e.*, to a solution of silver nitrate), he obtained silver chloride (= horn-silver) once more. What had happened?

In the first place, the silver chloride had suffered decomposition. Chlorine was liberated (but whether the *whole* of the chlorine or only a *part* of it is a question which has been debated ever since). Now when chlorine is liberated in water, and is at the same time exposed to sunlight, the chlorine decomposes the water, and oxygen gas is set free.

$$\begin{array}{ccccccc} Cl & + & H_2O & = & HCl & + & O \\ \text{Chlorine} & \textit{and} & \text{Water} & \textit{produce} & \text{Hydrochloric} & \textit{and} & \text{Oxygen.} \\ & & & & \text{acid} & & \end{array}$$

Of course only a very small quantity of hydrochloric acid is formed, and this remains dissolved in the water. The water being then added to a solution of silver nitrate we again get a chemical change—a double decomposition in fact—and silver chloride is once more formed.

$$\begin{array}{ccccccc} HCl & + & AgNO_3 & = & AgCl & + & HNO_3 \\ \text{Hydrochloric} & \textit{and} & \text{Silver} & \textit{produce} & \text{Silver} & \textit{and} & \text{Nitric} \\ \text{Acid} & & \text{Nitrate} & & \text{Chloride} & & \text{Acid.} \end{array}$$

In the second paragraph quoted above Scheele describes a confirmatory experiment. Let us represent his work by equations.

(1) He precipitates a solution of silver by sal-ammoniac.

$$\begin{array}{ccccccc} AgNO_3 & + & NH_4Cl & = & AgCl & + & NH_4NO_3 \\ \text{Silver} & \textit{and} & \text{Ammonium} & \textit{produce} & \text{Silver} & \textit{and} & \text{Ammonium} \\ \text{Nitrate} & & \text{Chloride} & & \text{Chloride} & & \text{Nitrate.} \end{array}$$

(2) He exposes the precipitate of silver chloride to sunlight.

$$\underset{\text{Silver chloride}}{\mathrm{AgCl}} \quad \underset{\textit{produces}}{=} \quad \underset{\text{Silver}}{\mathrm{Ag}} \quad \underset{\textit{and}}{+} \quad \underset{\text{Chlorine.}}{\mathrm{Cl}}$$

(3) He soaks the black powder (a mixture of unaltered silver chloride with black silver) in "caustic spirit of sal-ammoniac" (= ammonia). This is able to dissolve silver chloride; but a black powder remains undissolved.

(4) This black powder Scheele considers to be metallic silver, which has been set free by the action of light. To prove that it *is* silver he adds it to some "pure acid of nitre" (= nitric acid) by which it is dissolved.

$$\underset{\text{Silver}}{2\mathrm{Ag}_2} \quad \underset{\textit{and}}{+} \quad \underset{\text{Nitric Acid}}{6\mathrm{HNO}_3} \quad \underset{\textit{produce}}{=} \quad \underset{\text{Silver Nitrate}}{4\mathrm{AgNO}_3} \quad \underset{\textit{and}}{+} \quad \underset{\text{Water}}{3\mathrm{H}_2\mathrm{O}} \quad \underset{\textit{and}}{+} \quad \underset{\text{Nitrogen Trioxide.}}{\mathrm{N}_2\mathrm{O}_3}$$

(5) He finally adds sal-ammoniac to the "solution" so obtained.

$$\underset{\text{Silver Nitrate}}{\mathrm{AgNO}_3} \quad \underset{\textit{and}}{+} \quad \underset{\text{Ammonium Chloride}}{\mathrm{NH}_4\mathrm{Cl}} \quad \underset{\textit{produce}}{=} \quad \underset{\text{Silver Chloride}}{\mathrm{AgCl}} \quad \underset{\textit{and}}{+} \quad \underset{\text{Ammonium Nitrate.}}{\mathrm{NH}_4\mathrm{NO}_3}$$

Thus the circle is completed, and Scheele finished with the same substance (silver chloride) as he began with. From this he not unnaturally concluded that the effect of sunlight on silver chloride is to reduce it to metallic silver.

Guthrie Supports Scheele's Theory.—The first man to attempt to demonstrate, quantitatively (*i.e.*, by actually *weighing* the substances produced), the action of light upon chloride of silver was the late Professor F. Guthrie.* His results came near (but hardly sufficiently near) the actual results which should be obtained if silver chloride is completely decomposed by light into metallic silver and chlorine. He found that the silver chloride darkened rapidly when covered with pure and dry benzole (a liquid which contains no oxygen); and he writes: "The rapid blackening which the chloride here underwent proved the presence of oxygen to be unnecessary." This should be remembered in connection with the oxychloride theory of the latent image.

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* His original paper was published in 1857. It has been republished in the *British Journal of Photography* for 1885, p. 393.

The Latent Image not Destroyed by Nitric Acid.—A rather powerful argument *against* the theory that the latent image consists of metallic silver is furnished by the fact that the image is not destroyed when an exposed plate is bathed in the strongest nitric acid which can be used without affecting the gelatine.

Now nitric acid readily attacks and dissolves ordinary metallic silver; but it has no effect on silver chloride. It is found that if silver chloride be exposed to light in a vessel containing nitric acid, the chloride blackens readily. If the black substance formed be metallic silver one would imagine that it would be attacked by the nitric acid as rapidly as it was produced.

The Latent Image Considered as an Oxychloride, Oxybromide, or Oxyiodide.—The nature of the latent image early attracted the attention of that prolific worker, Robert Hunt. In his "Researches on Light" [*] he writes: "I am inclined to believe that the first action of the solar ray (upon silver chloride) is to liberate one-half the combined chlorine, which is very readily, moisture being present, replaced by oxygen.

"The absorption of oxygen, or rather its combination with the decomposing chloride, is proved by another very easy experiment. Some pure chloride of silver was arranged in a bent tube closed at one end, and the other end immersed in a bottle of distilled water. In this state the chloride was exposed for many days to the action of sunshine, during which time it was frequently shaken, for the purpose of exposing the whole of the powder to its influence. As the chloride darkened, the water rose into the tube, and it gave a precipitate of chloride of silver on the addition of the nitrate, thus appearing to prove the substitution of oxygen for chlorine under the agency of solar radiation. It was quite evident that some absorption of atmospheric air had taken place. This explanation will also serve for the iodide, bromide, and some other salts of this metal."

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[*] Second edition, 1854, p. 80.

Some thirty years after Hunt, the oxychloride theory was taken up by Dr. W. R. Hodgkinson, now Professor of Chemistry at Woolwich. He remarks:[*] "As a chemist only, reasoning from Abney's experiment with silver chloride in a perfectly dry state, that it undergoes no change on exposure to light, but only when water or substituted water is present, I thought it extremely likely that the colored substance was an oxychloride produced by the oxygen of a water molecule replacing chlorine in one or more molecules of silver chloride."

The probable chemical formula which Hodgkinson gives for the oxychloride is Ag_4Cl_2O; the corresponding formula for the oxybromide being Ag_4Br_2O; and for the oxyiodide, Ag_4I_2O.

In an ordinary dry-plate, the gelatine is far from being perfectly dry; there is moisture, moreover (water vapor), in the air which is in contact with the surface of the plate. The following formula will explain the chemical change which is believed to take place on the supposition that oxygen forms a part of the latent image:

$4AgBr$	+	H_2O	=	Ag_4Br_2O	+	$2HBr$
Silver Bromide	*and*	Water	*produce*	Silver Oxybromide	*and*	Hydrobromic Acid.

The hydrobromic acid set free probably combines with part of the gelatine.

The chief objection to this "oxygen" theory is that the silver haloids darken quite readily when exposed to light beneath liquids or gases which contain no oxygen, such as benzine or hydrogen. Of course it may be said that the dark "photo product" is in such a case different from that which we get under other conditions; but the weight of evidence is to the contrary.

On this question Bothamley remarks[†] "It is very difficult to believe that a silver oxychloride could form in presence of strong nitric or hydrochloric acid. It is also important to observe that the supposed oxychloride is not a reduction product of silver chloride, but a substitution product; the quantity of chlorine and oxygen in the formula given being sufficient to neutralize all the combining power of the silver. Silver oxide is known to be readily reduced to the metallic state by developers; and if we assume that this reducibility of the oxide is transferred to the oxychloride, which would be the case if the compound had the constitution represented by the formula given (Ag_4Cl_2O), the formation of the oxychloride would certainly explain the production of an image on development. On the other hand, it is equally well known that silver oxide is very readily attacked by acids, and it is not easy to see how an oxychloride could retain the instability of the oxide in presence of reducing agents, and yet offer so great a resistance to the action of acids. If further experiments prove that the darkened products are really an oxychloride and an oxybromide respectively, it is not at all probable that they will have the constitution which has been suggested.

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[*] *Photo. News*, 1887, p. 370; and 1888, p. 531.

[†] *Journal Camera Club*, 1890, p. 114.

CHAPTER XVI.

THEORY OF THE LATENT IMAGE (CONTINUED).

The "Sub-Salt Theory" of the Latent Image.—That great alchemist, Albertus Magnus, who flourished in the thirteenth century, refers to the black hue imparted to the human skin when it was rubbed with caustic silver (silver nitrate). Then his successor, Fabricius, in the middle of the sixteenth century, tells how the miners saw the mineral called "horn-silver" (silver chloride) darken on its transfer from the gloomy depths of the mine to sunlight. A century later, Glauber and Robert Boyle mention the darkening of silver compounds when long kept. But Schulze, in 1727, was the first who proved that this blackening was due to the agency of *light;* and his experiments were confirmed by Beccarius, of Turin (about 1750), and by Scheele (1777), the latter chemist being the first to attempt to investigate the nature of the change produced.

Taking silver chloride as an example, we may consider the following facts as certain:

(1) A short exposure to light gives a "latent image," invisible to the eye, but capable of being developed into a visible image.

(2) A longer exposure to light causes the white silver chloride to change color, first to violet and then to brown. This dark-colored product is probably identical with that which forms the latent image. We cannot *see* the molecules of altered silver chloride which form the latent image, any more than we can see a few small leaden shots scattered over a sackful of flour. But the *continued* action of light increases the number of the altered molecules, and they then become visible.

(3) The exposed silver chloride gives off a part or the whole of its chlorine, which can be collected and tested in the usual way.

(4) The action of light upon silver chloride is greatly accelerated by the presence of some substance able to combine readily with chlorine. Such a substance is called a "sensitizer."

(5) In the absence of all sensitizers or chlorine absorbents (as in a vacuum) pure silver chloride is *not* affected by light.

(6) Exposure to the vapors of chlorine, bromine, or any compound which will readily part with these elements, *destroys* the latent image.

The other haloid salts of silver—the bromide and the iodide—when exposed to light are similarly affected to the chloride.

All these considerations help us to believe that the action of light upon these compounds of silver in producing a latent image is of a *chemical* and not of a physical nature.

The point which has to be determined is this: What is the chemical nature of the dark-colored material produced by the agency of light? To this it may seem strange to say that we are not yet able to return a positive answer. Although the whole of the silver salt may appear to be converted by many days' exposure and by frequent shaking into the dark material, yet this change is superficial only. The outside of each tiny particle suffers change; but the inner and greater portion remains unaltered.

The "sub-salt" theory which we have now to describe has in past years received the powerful support of Dr. H. Vogel, and of Captain Abney. The chemistry of the sub-salts of silver is obscure and difficult. If there are such compounds, then one of them should be the sub-oxide of silver, having the formula Ag_4O. The German chemist, Wöhler, believed that he had obtained such a compound in 1839, but the later researches of Newberry, Muthmann, Von Pfordten, Bailey, and Fowler go to show that Wöhler must have been mistaken. Still, the existence of the sub-oxide is not necessary to the latent image theory, which declares that the effect of light upon silver chloride is to reduce it to the state of silver sub-chloride:

$2AgCl$	$=$	Ag_2Cl	$+$	Cl
Silver Chloride	*produces*	Silver Sub-chloride	*and*	Chlorine.

The iodide is similarly reduced to the sub-iodide:

$2AgI$	$=$	Ag_2I	$+$	I
Silver Iodide	*produces*	Silver Sub-iodide	*and*	Iodine.

And the bromide, in its turn, is reduced to sub-bromide:

$2AgBr$	$=$	Ag_2Br	$+$	Br
Silver Bromide	*produces*	Silver Sub-bromide	*and*	Bromine.

It will be seen that this theory fits in nicely with the observed facts. It explains why the presence of a sensitizer is necessary—to absorb the haloid given off under the action of light. In the absence of some such absorbent, we can imagine that light still decomposes the silver salt; but the liberated halogen at once *recombines* with the sub-salt so formed, bringing it back to its original condition:

Ag_2Cl	$+$	Cl	$=$	$2AgCl$
Silver Sub-chloride	*and*	Chlorine	*produce*	Silver Chloride.

That such a decomposition and recombination can take place was shown by Morichini, who found that when moist silver chloride was exposed to light in a sealed glass tube, *in vacuo*, it rapidly blackened; but that the white color was restored when the tube was kept in a dark place for a few days.

Another—and perhaps more feasible—idea is that the light is unable to effect the decomposition, unaided. But when some substance (sensitizer) is present which exerts an attraction upon the haloid, then the *combined* effect of light plus chemical attraction effects a separation or decomposition.

Arguing from analogy, we might expect silver sub-chloride to exist; for the metals, copper and mercury—which have many points of resemblance to silver—both form sub-chlorides. Thus with copper we have—

Copper chloride	$CuCl_2$
Copper sub-chloride	$CuCl$

And with mercury—

Mercury chloride (*corrosive sublimate*)	$HgCl_2$
Mercury sub-chloride (*calomel*)	$HgCl$

The metal *thallium*, discovered by Mr. Crookes in 1861, also forms a double series of chlorides—

Thallium trichloride	$TlCl_3$
Thallium monochloride	$TlCl$

But all these are well-known chemical compounds, easily prepared. They are all *white.* Again, if an oxidizing agent be present they cannot be formed. Now we know that the substance which it is proposed to call silver sub-chloride is of a dark color, and is formed even when the silver chloride is exposed to light beneath the surface of such a powerful oxidizing agent as nitric acid. The action of light upon mercury sub-chloride is to decompose it into mercury chloride and metallic mercury; and not to change it to any lower chloride:

$$\begin{array}{ccccc} 2HgCl & = & HgCl_2 & + & Hg \\ \text{Mercury} & \textit{produces} & \text{Mercury} & \textit{and} & \text{Mercury.} \\ \text{Sub-chloride} & & \text{Chloride} & & \end{array}$$

The summing-up of the whole matter is, that the evidence clearly proves that silver chloride* loses chlorine on exposure to light; but that it has not yet been certainly proved that the blackened residue is silver sub-chloride, Ag_2Cl, and nothing else.

We may add that it is a fact well known to plate-makers that spoiled plates (coated with silver bromide in gelatine), when stacked in an open space exposed to light give off an odor which—so far as the sense of smell is concerned—is indistinguishable from that of bromine.

The Latent Image as a "Lake"—Carey Lea's "Photo Salts."—The distinguished American photo-chemist, Mr. Carey Lea, was born at Philadelphia in 1823. English readers made his acquaintance in 1864, when he commenced to act as correspondent for the *British Journal of Photography*, and his name has ever since been a "household word" among those who have studied photography mainly for the many captivating problems which it offers in chemistry and in physics.

Of all Mr. Lea's researches none equal in interest and importance the series upon the "photo salts of silver," and upon "allotropic silver," which appeared during the years 1887–91 in the *American Journal of Science;* and which were reprinted on the English side of the Atlantic in the *Philosophical Magazine*, and in the *British Journal of Photography*, etc.

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* And the chloride stands as a type also for the bromide and the iodide.

In the opening paper of the series it is declared that the object is to show: "(1) That chlorine, bromine, and iodine are capable of forming compounds with silver exhibiting varied and beautiful coloration, pearl-blossom, rose, purple, and black. That these compounds (except under the influence of light) possess great stability; that they may be obtained by purely chemical means, and in the entire absence of light.

"(2) That of these substances the red chloride shows a tendency to the reproduction of colors.

"(3) That these substances, formed by purely chemical means, constitute the actual material of the latent or invisible photographic image; which material may now be obtained in the laboratory without the aid of light and in any desired quantity. They also form part of the visible product resulting from the action of light on the silver haloids."

According to this theory, when light acts upon an ordinary gelatine dry-plate, some of the silver bromide ($AgBr$) is reduced to the state of sub-bromide (Ag_2Br), but it is only possible for the light to form a small quantity of the sub-bromide. The sub-bromide then enters into a molecular combination with the unaltered silver bromide, to form a purplish compound of a nature similar to what is called a "lake." Such a compound of silver sub-bromide and silver bromide Lea calls a "photo-bromide." Similarly, we get a "photo-chloride" and a "photo-iodide," when silver chloride and silver iodide are respectively exposed to light. Collectively, they may be termed "photo-salts," as being capable of production by the action of light. Such compounds—unlike the normal sub-salts—are not attacked by strong cold nitric acid.

With silver chloride Lea found that it was not possible to convert more than about 8 per cent. of the material into the sub-chloride. The black photo-chloride is easily obtained by treating reduced silver with two or three applications of sodium hypochlorite.

The identity of the photo-salts with the material which composes the latent image is shown by the following facts: 1st, in the entire absence of light, sodium hypophosphite is able to affect a sensitive film of silver haloid in the same way as does light, *producing a result equivalent to a latent image formed by light*, and capable of development in the same way as an actual impression of light.

2ndly. That these two effects, the impression produced by hypophosphite and that by light, comport themselves to reagents in exactly the same way, and seem every way identical.

3rdly. That the image produced by the action of the hypophosphite on silver chloride always gives rise to a positive on development; but on silver bromide may give rise to either a direct or a reversed image, *both of these effects corresponding exactly with those of light.* More than this, sodium hypophosphite may be made to reverse the image produced by *light* on silver bromide; and conversely light may be made to reverse the action of *hypophosphite.* So exact a correspondence in these remarkable properties can scarcely be fortuitous.

It is an interesting experiment to damp the surface of a wood printing-block with sodium hypophosphite. Then in the dark-room place the block in contact with the surface of a gelatine dry-plate. On development in the ordinary way, the plate gives the picture which was carved upon the block. Alkaline solutions of milk-sugar or of grape-sugar, or a solution of ferrous hydrate produce the same effect as sodium hypophosphite. The "photo-products" (this term seems better than "photo-salts," as the latter would infer that the bodies in question have a definite chemical composition) so formed are affected similarly to the latent image; being destroyed by potassium bichromate, and decomposed by sodium hyposulphite and by ammonia.

It is to be noted that nitric acid, which attacks either silver alone, or silver chloride alone, or silver sub-chloride alone, has no effect upon the mixture (or rather molecular combination) of these substances which is produced by the action of light upon silver chloride. Lea writes:—"The principal action of light on AgCl (precipitated in presence of excess of hydrochloric acid) consists in the formation of a small quantity of sub-chloride, which enters into combination with the white silver chloride not acted upon, forming the photo-chloride, and thus is able to withstand the action of strong nitric acid. At the same time a trace is formed, either of metallic silver or of uncombined sub-chloride, it is impossible to say which. After a certain very moderate quantity of photo-chloride is formed, the action of light seems to cease.

"The nature of the product formed by the continued action of light on silver chloride, seems to support the conclusion that the sub-chloride is combined with the whole of the normal chloride after the manner of *lakes* rather than in equivalent proportions."

The term "lake" is applied in commerce to certain colored compounds which consist of organic coloring matters precipitated in the presence of alumina. No definite chemical compound is formed, but the two substances hold so firmly together that they cannot be separated by repeated or long-continued washing. Probably some kind of molecular combination takes place.

Summing up Carey Lea's theory of the latent or photographic image we note that, according to him, it consists neither of the normal silver haloid physically modified, nor of a sub-salt; but of a combination of normal salt and sub-salt. That the sub-salt loses in this way its weak resistance to reagents, and acquires stability, thus corresponding to the great stability of the latent image, which, though a reduction product, shows considerable resistance to even so powerful an oxidizer as nitric acid.

The Latent Image Consists of Allotropic Silver Bromide—Leaper, 1891.—We have quoted in tabular form the different varieties of silver bromide, as classified by De Pitteurs. Commencing with the variety of AgBr which transmits orange light, we find that by the addition of energy in the form of heat we can steadily increase the sensitiveness of the silver bromide to light, until at last we arrive at a form of AgBr which transmits blue rays, and which is itself exquisitely sensitive to light.

By *continuing* to heat the emulsion after having reached this point, we obtain a form of AgBr which is sensitive to *red* light, and which is at once decomposed by a developer, without having been exposed to light at all, the plate being—as we say—"fogged all over."

Leaper argues * that the effect of energy in the form of *light* is similar to its effect in the form of heat. By light, the seventh allotropic form of AgBr shown in De Pitteurs' table is converted into the eighth and last modification shown in the same table. The former is not affected by our developers, the latter is; an image can therefore be developed upon such a plate.

TABLE OF THE CHEMICAL THEORIES OF THE LATENT IMAGE.

I.—The Latent Image consists of Metallic Silver..	Scheele, 1777. Guthrie, 1857, etc.
II.—The Latent Image an Oxy-Haloid Salt of Silver..	Hunt, 1854. Hodgkinson, 1887.
III.—The Latent Image a "Sub-Salt" of Silver....	Vogel. Abney.
IV.—The Latent Image a "Lake."...............	Carey Lea, 1887.
V.—The Latent Image composed of Allotropic Silver Haloid....................................	Leaper, 1891.

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* *British Journal of Photography*, 1891, p. 231.

CHAPTER XVII.

PHYSICAL THEORIES OF THE LATENT IMAGE.

A *physical* change in matter is one by which the chemical composition of the substance remains unaltered, although some of its physical properties, as its color, taste, etc., are changed.

Light is able to produce physical changes in certain kinds of matter. When lumps of red *realgar* (arsenic disulphide, As_2S_2) are exposed to light, they crumble away to a yellow powder. But by simply fusing this powder it is restored to the state of red lumps as before. Chemical analysis shows that the yellow powder and the red lumps have precisely the same chemical composition (As_2S_2). The change of color is probably due to some rearrangement of or in the molecules of the realgar.

Half a century ago, M. Moser, of Konigsberg, detailed* some remarkable experiments, which were repeated and extended by Draper,† showing that if any clear, hard surface, as of metal or glass, be covered with a perforated screen and then exposed to light, an image of the screen can be subsequently produced by removing the screen and *breathing* upon the bare glass. The water-vapor in the breath condenses most upon the parts which have been exposed to light.

I. *Latent Image due to Molecular Change Effected by Light —Hardwich*, 1855.—The theory of production of a latent image stated by Hardwich ‡ in 1855 is illustrated by a diagram, which we reproduce:

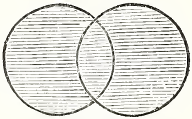

FIG. I.

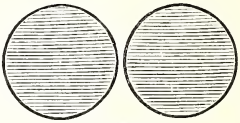

FIG. 2.

Here Fig. 1 represents a molecule of ordinary silver iodide, the component atoms of silver and of iodine being closely associated, and having much chemical attraction for one another.

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* *Journal of the Academy of Sciences* (Paris), for 18th July, 1842, etc.

† *Philosophical Magazine*, for September, 1840.

‡ Page 109, "Hardwich's Chemistry," by Taylor. 9th Ed.

Fig. 2 represents the same molecule, after it has been acted upon by light. The atoms are now separated so that they only just touch, and their mutual attraction is much weakened. The consequence of this weakening is that a solution (as a developer) which has no effect upon the ordinary silver iodide, is able to decompose the same substance after it has been acted upon by light.

The weakness of this theory lies in the fact that *pure* silver iodide (or any other haloid salt of silver) is *not* affected in this way by light *if it be exposed to light in a vacuum*

II. *The Latent Image Considered as a Vibration of the Atoms.*—It is evident that any cause which weakens the force by which the atoms forming a molecule are held together, will render that molecule more easy to be decomposed. Physicists and chemists agree in believing that not only are all the molecules of all matter in constant motion (this molecular motion we know as *heat*), but that the *atoms* composing each molecule are themselves moving or vibrating. If this atomic vibration be greatly increased, it may be sufficient to cause the molecules to "shake themselves to pieces," and chemical decomposition then takes place. Thus by heat alone we are able to decompose the red oxide of mercury into mercury and oxygen.

HgO	$=$	Hg	$+$	O
Oxide of Mercury	*produces*	Mercury	*and*	Oxygen

But if the motion of the atoms be only increased to a certain extent, the effect may be that their affinity for each other will be just so much weakened as to allow of their decomposition by solutions (developers) which normally would have no effect upon them.

Suppose we compare the two atoms which compose a molecule of silver bromide ($AgBr$) to two balls united by a short piece of India-rubber. Let the normal condition of the balls be that of revolution round a point midway between them, just enough to keep the rubber stretched. Let the motion of the balls be now increased. The result will be that more tension will be put on the rubber, the balls will move farther apart and a *less* force will be required to cut the connecting link and so separate the balls entirely, than if they were in their normal state.

When molecules of the silver haloids are exposed to light, the advocates of the "vibratory theory" believe that the motion of their atoms is increased, and that their subsequent decomposition by a developer is thus facilitated.

The physical theory, in one form or another, of the latent image, was first advanced by Moser, to whose experiments we have already alluded; it was supported by Hardwich, and by Dr. D. Van Monckhoven; * at one time Mr. Carey Lea was its principal advocate,† though his later work has led him to renounce it. Light is a form of energy which travels through space in the form of ether waves. When these waves fall upon the silver haloids the molecules of the latter are thrown into a state of unstable equilibrium, and are then readily affected by chemical solutions (developers) which would otherwise be powerless to decompose them.

Objections to Physical Theories of the Latent Image.—If the latent or "photographic" image consists merely of the same substance as the unaltered silver salt, but in an abnormal condition as regards the position or vibration of its atoms or molecules, it is difficult to conceive how that abnormal position is *maintained*. Dry-plates have been exposed, and then kept for several years before development, without the resulting image showing any lack of vigor. Is it possible that any unstable condition or vibration could have been maintained during so long a period? Such a thing is not, however, impossible. In our own experience as a microscopist and geologist, we have frequently obtained thin slices of igneous rocks in which were cavities (visible only under the microscope) partly filled with some liquid, through which a bubble of gas moved with rapid speed backwards and forwards. The time since the rocks in question consolidated, and the bubbles were imprisoned, must be reckoned by millions of years. Yet the bubbles have probably been in continuous motion ever since!

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* *British Journal of Photography* for 1863, p. 74.

† *British Journal* for 1865-66-67, numerous articles.

But the case is very different with molecules of silver bromide embedded in a tough solid like gelatine; and all analogy would lead us to expect that if the latent image consisted merely of a vibratory movement of the atoms, or of an abnormal condition of the molecules, that it would speedily disappear; and that the plate would then be restored to its pristine state.

It was formerly believed that the latent image *did* disappear when the exposed plate was kept for a few months. And in the case of an exposed daguerreotype plate, especially, this is found to be the case. But in all such cases the plate has suffered from the impurities always present in the atmosphere, from which it is found impossible to preserve the plate unless it be hermetically sealed up in a vacuum. Moreover, every film contains small quantities of substances which we can only consider as "dirt" (because it is "matter in the wrong place") and these substances combine with and destroy the latent image.

In the case of the daguerreotype, the silver plate is sensitized by exposing it to the vapor of iodine. Now there is always present upon the plate an *excess of iodine.* If the action of light be—as we presently hope to prove—of a *chemical* nature, consisting in the separation of part of the iodine contained in the silver iodide, then we have present in this free iodine a substance, which is able to combine with the partly reduced silver iodide and so to restore it to the state of normal iodide.

Ag_2I	$+$	I	$=$	$2AgI$
Silver Sub-iodide	*and*	Iodine	*produce*	Silver Iodide.

Thus the fading of the latent image, in the case of the daguerreotype at all events, may be taken to be as much in favor of the chemical as ot the physical theory of the latent image.

Starnes' Hypothesis of the Latent Image.—Light Ruptures the Gelatine Casing.—A second physical hypothesis for explaining nature of the latent image was broached by Mr. H. S. Starnes, in 1883.* He urged "that light, acting on the salts of silver, when held in suspension in collodion or gelatine, has a previous mechanical action, namely, the rapid vibration or expansion of the particles, which strain or burst the protecting cells of the collodion or gelatine." It is certain that the gelatine of an emulsion protects and wraps round the molecules of silver bromide; for certain chemical solutions, which will decompose silver bromide when alone, produce no effect when poured upon an ordinary dry-plate. Again, if an emulsion of silver bromide in gelatine be exposed to light, and then *re-melted*, it will show but the merest trace of fog on development. Starnes reasons, that in a dry-plate every molecule of silver bromide is surrounded and protected by a coating of gelatine. The action of light *ruptures* the gelatine, and thus exposes the silver salt to the action of the developer.

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* *British Journal of Photography*, vol. xxx., pp. 643, 656; vol. xxxi., pp. 501, 712.

Objections to this theory are: (1) that by soaking an exposed plate in a solution of bichromate of potash the latent image is *destroyed*. Now, how could the bichromate repair the breaches which Starnes supposes to be made by light in the gelatine?

(2) According to this theory, silver bromide in collodion should be as sensitive to light (or more so) than the same salt embedded in gelatine, for collodion forms a more porous and delicate film than the tough gelatine. Yet the contrary is the case.

(3) The latent image is destroyed by a solution containing bromine. This solution attacks the gelatine; and, under Starnes' theory, one would imagine that it would intensify—so to speak—the action of light, instead of destroying it.

Electrical Theory of the Latent Image.—The idea that electricity might have something to do with the production of the latent image has naturally occurred to many minds. Its possibility has of late been brought forward by Dr. T. W. Drinkwater; and a series of remarkable experiments by Professor Minchin have also been lately published * which point in the same direction.

An early work of great interest is Becquerel's book, "La Lumiere; ses causes et ses effets," written about half a century ago.

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* *Journal of the Camera Club*, for April, 1891.

The researches of the last few years have shown that electricity has a velocity comparable, if not identical, with that of light (186,000 miles per second); and, further, that electricity comes from the sun in company with light. We know, too, that electricity travels in *waves*, just as light is known to do. One of Becquerel's experiments was to coat two silver plates with chloride of silver and place them in a vessel of water, connecting them by wires with a delicate galvanometer.* When *one* of the plates was exposed to light, a current of electricity was invariably produced. Blue and ultra-blue light produced this effect; but not red, yellow or green. Professor Minchin's experiments go much further in the same direction; but the subject is very complex and much yet remains to be done.

Latent Image Produced by Pressure.—In 1885 Carey Lea observed † that when any hard substance was pressed upon or drawn over the surface of a film sensitive to light, that an effect was produced which—although quite invisible to the eye—could be "developed" by the same solutions as brought out the latent image produced by exposing to light.

The same effect was investigated by Captain Abney in 1883–4.‡ If we write upon the surface of dry-plates (of course in ruby light only) with the rounded end of a glass rod, the letters formed will stand out in black when a developer is applied to the plate Any hard material may be used instead of glass, and the effect is transmitted through paper, if a sheet of that substance be interposed between the rod and the film. The image so formed behaves similarly to the latent image produced by light (being destroyed by potassium bichromate) and is probably identical with it. It appears to lie at the bottom of the film, next the glass.

The recent investigations made by the Belgian chemist. Professor Spring, show that chemical changes are produced in many mixtures when they are submitted to great pressure. And when a sensitive film is submitted to "shearing stress" or pressure, it is probable that a decomposition of the silver haloid is brought about, which is revealed when the film is submitted to the action of a developing solution.

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*An instrument for detecting the occurrence of an electric current.

†*British Journal of Photography*, vol. xiii., p. 84.

‡*Journal of the Photographic Society of Great Britain.*

TABLE OF PHYSICAL THEORIES CONCERNING THE LATENT IMAGE.

1.—The Latent Image due to a Molecular Alteration in the Silver Haloid	Moser, 1842. Hardwich, 1855.
II.—The Latent Image due to Vibration of Atoms	Carey Lea, 1865.
III.—The Latent Image due to Rupture of Gelatine Casing	Starnes, 1883.
IV.—Electrical Theory of the Latent Image	Drinkwater, 1888.
V.—A Latent Image Can Be Produced By Pressure	Carey Lea, 1866. Abney, 1883.

SUMMARY OF THE WHOLE QUESTION OF THE LATENT IMAGE.

The facts point conclusively in the direction of some *chemical* change. Probably the hypothesis of Carey Lea, that the latent image is a molecular combination of the nature of a "lake," accounts better for the observed facts than any other theory.

SOME IMPORTANT PAPERS ON THE NATURE OF THE LATENT IMAGE.

PHOTOGRAPHIC NEWS:

1887.—*Hodgkinson, Dr. W. R.*—The Chemistry of the Latent Image; p. 370.

1888.—*Hodgkinson, Dr. W. R.*—Lowest Stages of Combination of Silver; p. 531.

——. *Drinkwater, Dr. T. W.*—Some Notes on the Nature of the Latent Image; p. 390.

1890.—*Spiller, J.*—The Chemical Phenomena of Light (Dr. Percy and G. Shaw); p. 256.

—— *Meldola, Professor R.*—The Photographic Image; pp. 557, 580, 599.

BRITISH JOURNAL OF PHOTOGRAPHY:

1887.—*Lea, M. Carey.*—Photo-Salts of Silver; pp. 330, 345, 472, 486, 522.

1888.—*Gifford, H. J.*—Notes on the Nature of the Latent Image; p. 403.

1889.—*Braham, P.*—Light, its Chemical Action; p. 92.

—— *Wiggin, J. C.*—The Chemistry of Photography; p. 348.

—— *Bedding, T.*—Continuating Action of Light; p. 619.

—— ———— The Negative Image; pp. 684, 716, 732, 776.

—— *Lea, M. Carey.*—Allotropic Forms of Silver; pp. 444, 461, 478, 494, 575, 621, 638, 814.

1890. *Hitchcock, R.*—Action of Light on Silver Chloride; pp. 8, 66, 188, 222, 301.

—— *Bothamley, C. H.*—The Latent Photographic Image; pp. 235, 243, 248.

—— *Brebner, H.*—Nature of the Invisible Image; pp. 487, 551, 617, 631, 649, 682.

1891.—*Lea, M. Carey.*—Allotropic Silver; pp. 229, 262, 627, 726.

—— *Leaper, C. J.*—New Theory of the Developable Image; p. 231.

Sutton's Photographic Notes:

1856.—*Frankland, Dr. E.*—On the Chemical Changes occurring in Photography; Vol. I., Nos. 5, 6, and 7.

Chemical Society's Quarterly Journal:

1857.—*Guthrie, Fred.*—On the Action of Light upon Chloride of Silver; Vol. X., Part I. (Reprinted in *British Journal of Photography* for 1885, p. 393.)

CHAPTER XVIII.

THE CHEMISTRY OF DEVELOPMENT.—(I.) DAGUERREOTYPE PROCESS.

What is Development? By "development," in photography, we understand the *making plainly visible* of any image which was previously invisible, or at all events scarcely discernible.

When a sensitive surface, as that of a dry-plate, is exposed to light within the camera, an image, called the latent, invisible, or photographic image, is impressed upon it. This image is not visible upon the surface of the plate. But by applying to the plate certain solutions, called "developers," the image is made visible.

It is plain that a developer must be some substance which acts *differently* upon the parts of the sensitive surface which have been affected by light, as compared with those which the light has *not* affected. By this differential action the *contrast* between the exposed and unexposed parts is *increased*; and the latent image then becomes the visible or developed image.

The First Man who Developed a Plate.—The first man who has a real claim to be considered a "photographer" was Joseph Nicéphore Niepce, of Chalon-sur-Saone, in France. He was the first to take a picture in the camera; the first to develop a plate; and the first to secure a permanent photograph. He was about forty-eight years of age when he commenced (in 1813) to work at the problem of securing pictures by the agency of light. By the year 1827 he had certainly achieved considerable success, for in that year he paid a visit to his brother Claude (then residing at Kew, in England), bringing with him several specimens of his work. He did not divulge his method, but some of his "photographs," which he presented to certain of his friends in England, are now in the British Museum, and are very creditable indeed. He labored in vain to perfect his discovery; entered into partnership with Daguerre in 1829; and died, a disappointed man, in 1833, aged sixty-eight.

How Niepce Developed his Plates.—Niepce coated metal plates with bitumen, dissolved in oil of lavender. By an exposure in the camera for several hours, a latent image was impressed on these plates. But the process was too slow for camera work, and most of Niepce's specimens were procured by contact-printing—an engraving (rendered transparent by varnishing) being laid upon the bitumenized plates, and the whole then exposed to sunlight.

The effect of sunlight is to *oxidize* the bitumen; oxygen, from the air, combining with the bitumen to form complex organic compounds whose precise chemical nature it is impossible to determine. Such oxidized bitumen is harder, and is insoluble in liquids, such as oil of lavender and petroleum, which readily dissolve bitumen which has not been exposed to light. It is only necessary, therefore, to soak or wash the exposed plate with some bitumen solvent, in order to remove the unacted-on bitumen, while the insoluble remains, forming the "high-lights" of the now visible picture.

A letter from Niepce to Daguerre is in existence, bearing the date 5th December, 1829, in which the phenomena of development are graphically described:—

"The plate (which had been coated with bitumen) may be immediately submitted to the action of light in the focus of the camera. But even after having been thus exposed a length of time sufficient for receiving the impressions of external objects, nothing is apparent to show that these impressions exist. The forms of the future picture remain still invisible. The next operation then is to disengage the shrouded imagery, and this is accomplished by a solvent, consisting of one part by volume of essential oil of lavender and ten of oil of white petroleum. Into this liquid the exposed tablet is plunged, and the operator, observing it by reflected light, begins to perceive the images of the objects to which it had been exposed gradually unfolding their forms. The plate is then lifted out, allowed to drain, and well washed with water."

Many millions of plates have been developed since the days of Niepce; but probably no man has witnessed the "modern miracle" with such joy, wonder, and surprise as he whose eyes *first* saw the invisible image made visible.

The method of development necessary in heliography, or Niepceotype, is a *physical* method. It depends on a difference in solubility between two substances—oxidized and unoxidized bitumen.

Daguerre's Method of Development.—Once an idea has been communicated, a principle established, or a fact demonstrated, the thing becomes familiar and more discoveries are sure to follow. Daguerre repeated the work of Niepce, and so the development of a latent image became a familiar idea to him; but he failed to attain the necessary *rapidity* which he rightly recognized as indispensable to commercial success in photography, and so he experimented in every direction, trying to secure this indispensable factor.

Daguerre appears from his early correspondence with Niepce, about 1828, to have always had an inclination for the use of *iodine* in his photographic experiments. Niepce had used the same substance in conjunction with metal plates, but without success. After the death of Niepce, in 1833, Daguerre continued to work at the problem.

The exact date cannot be fixed, but it was probably in or about 1836 that a "happy accident" is said to have rewarded the French scene-painter for all his toil and trouble.

It appears that Daguerre discovered that silver iodide, formed and exposed upon a plate of silver, was sensitive to light. In this case the metallic silver at the back of the silver iodide acts as a sensitizer, absorbing and chemically combining with the iodine liberated by light. It has even been shown by Carey Lea that silver iodide can act *as its own sensitizer.* We may perhaps suppose that a higher iodide of silver exists, in which case the following equation would represent the fate of the iodine liberated by light:

$$\underset{\text{Silver Iodide}}{AgI} \underset{\textit{and}}{+} \underset{\text{Iodine}}{2I} \underset{\textit{produce}}{=} \underset{\text{Silver Ter-Iodide.}}{AgI_3}$$

Be this as it may, Daguerre found that by a *prolonged* *exposure in the camera* he obtained a faint printed-out image of objects in bright sunshine, in about two or three hours. This was no more rapid than poor Niepce's work with bitumenized plates, or than the similar results which Fox Talbot was at the same time (1835–39) obtaining in England upon paper coated with silver chloride. But fortune favored Daguerre. One day he removed from his camera an iodized silver plate which, although it had been exposed in the usual way, showed no visible sign of an image. It was, as we should say, "greatly under-exposed." This plate Daguerre put away in the cupboard in which he kept his chemicals. Going to this cupboard the next day, Daguerre was surprised, and doubtless much pleased, to see that the face of the iodized silver plate was no longer blank, but that it bore a good image of the objects towards which the lens of the camera in which it was exposed had been directed. The plate had, in fact, been *developed* during the night. But how, and by what? A study of the contents of the cupboard revealed an open dish of mercury, upon or close to which the under-exposed plate had been laid.

Further experiments were quickly made; and it was found that mercury vapor possessed the marvelous power of bringing out or developing the latent image on an iodized silver plate which had received only from ten to thirty minutes' exposure within the camera. By *warming* the mercury in a small iron pot, over which the exposed silver plate was suspended, iodized side downwards, the speed of development was increased so that instead of requiring "all night" (as in Daguerre's cupboard) the operation was completed in a few minutes.

The development of a daguerreotype belongs to the *physical* class. We can conceive of the exposed plate over the warm mercury as being subjected to a bombardment of millions of molecules of mercury all over its surface. The portions of the plate affected by light are able to combine or amalgamate with this mercury; but from the unaffected parts the mercury molecules bounce back again. The latent image is thus built up or developed by the accretion of mercury molecules. Professor Meldola has well compared the action to the effect of a sand-blast upon a sheet of glass on which a design has been painted in gum. The particles of sand which strike the gummy parts adhere to them, and so a design is "developed" in sand particles. As to the *reason* why the molecules of mercury combine only with the portions of the plate which have been affected by light, we know little or nothing. The action may be chemical—some definite compound being formed between the mercury and the "photo-salt" or reduction product; or (more probably) it may be merely physical, the mercury being able to amalgamate with the sub-iodide of silver, but not with the normal silver iodide.

It is possible to (temporarily) develop a daguerreotype plate by simply breathing upon it. The photo-reduction product attracts, or rather combines, with the moisture, just as it attracts the mercury.

CHAPTER XIX.

CHEMISTRY OF DEVELOPING PROCESSES.—(II.): CALOTYPE AND WET COLLODION.

Chemistry of Calotype Development.—It must, we think, be granted, that if the *original* processes for photography published (1) by Daguerre, and (2) by Fox Talbot in the year 1829, be compared, the advantage lies on the side of the Frenchman; and this because he had discovered a process of *development*, while Talbot's "photogenic drawings" were necessarily *printed out* in the camera.

But in September, 1840, Talbot discovered a method of development which placed his process practically on a level with that of his foreign rival. The same process of development was discovered, independently, in the same year by an English clergyman, the Rev. J. B. Reade.

Talbot named his new method the *Calotype*, and he patented it early in 1841.* His sensitive surface consisted of sheets of paper coated with silver iodide which, when it was desired to prepare them for use, were brushed over with a mixture of silver nitrate, gallic acid, and acetic acid. To this mixture the name of "gallo-nitrate of silver" was applied. After exposure in the camera, the image was either invisible or very faint; it was then brought out, strengthened, or "developed" by pouring over it more of the "gallo-nitrate of silver" solution, to which some alcohol was usually added in order to cause it to flow freely over the plate.

Here we have a developer containing three ingredients. Let us consider its chemical action, and the use of each ingredient.

Pure gallic acid was first obtained by Scheele in 1786. Its molecule contains eighteen atoms, $C_7H_6O_5$. It eagerly combines with oxygen, and with the halogens; and is therefore styled a "powerful reducing agent."

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* The exact date was February 8, 1841. This was the third British patent taken out in connection with photography.

The silver nitrate, to begin with, acts as a sensitizer, combining with the iodine which is given off under the agency of light. Let us first represent the decomposition of the iodide of silver when lights acts upon the sensitive plate:

AgI	$=$	Ag_2I	$+$	I
Silver Iodide	*produces*	Silver Sub-iodide	*and*	Iodine.

The silver nitrate then attracts and combines with the liberated iodine:

$6AgNO_3$	$+$	$6I$	$+$	$3H_2O$	$=$	$5AgI$	$+$	$6HNO_3$	$+$	$AgIO_3$
Silver Nitrate	*and*	Iodine	*and*	Water	*produce*	Silver Iodide	*and*	Nitric Acid	*and*	Silver Iodate.

The latent image is thus formed of silver sub-iodide, Ag_2I. Now this silver sub-iodide has a greater attraction for, or is better able to combine with, nascent or freshly liberated silver, than the silver iodide which constitutes the surface of the film where it has *not* been affected by light.

What has to be done then is to produce metallic silver upon the surface of the film. There must also be a layer of water upon the surface to hold the chemicals in solution, and to allow the attracted atoms of silver to move freely towards the attracting molecules of silver sub-iodide.

By applying to the surface of the film a mixture of silver nitrate and gallic acid only, we get a copious, indeed too copious, production of metallic silver. The result of this would be a deposit of silver *all over* the plate, by which it would be "fogged" and spoilt. Here comes in the use of the acetic acid. This substance acts as a *restrainer*, retarding the precipitation of the silver, and giving time for the sub-iodide to exercise its attractive influence, so allowing this sub-salt to draw to itself all the silver atoms as rapidly as they are produced.

$C_6H_2(HO)_2.COOH$	$+$	$2AgNO_3$	$+$	H_2O	$=$	Ag_2	$+$	$2HNO_3$	$+$	$[C_6H_2(HO)_3.COOH+O]$
Gallic Acid	*and*	Silver Nitrate	*and*	Water	*produce*	Silver	*and*	Nitric Acid	*and*	Oxidized Gallic Acid.

Chemical Action of Development in the Wet-Collodion Process.—In the wet-collodion process, as published by F. S. Archer, in 1851, the developer was composed of

Water	1 ounce
Acetic acid	1 drachm
Pyrogallic acid	3 grains

Archer claimed that "the great power of pyrogallic acid in bringing out the latent image was first made known by me in a short description in the May number of *The Chemist*, for 1850." Pyrogallic acid was discovered by Braconnot, in 1831; and Professor Meldola writes that "its use as a photographic developer was suggested in 1851, by Liebig and Regnault." He seems, therefore, to have overlooked the claims of Archer. It is obtained by strongly heating gallic acid, when carbonic acid is given off:

$$\underset{\text{Gallic Acid}}{C_6H_2(HO)_3CO_2H} \quad \underset{\textit{produce}}{=} \quad \underset{\text{Pyrogallic Acid}}{C_6H_3(HO)_3} \quad \underset{\textit{and}}{+} \quad \underset{\text{Carbonic Acid Gas.}}{CO_2}$$

Archer's developer, as given above, appears to contain only two ingredients, pyro and acetic acid, but a third and very necessary part consisted of the solution of nitrate of silver with which the surface of the wet-collodion plate was covered, both during exposure and development, and which it derived from the bath of silver nitrate into which it was plunged just before exposure.

This silver nitrate was reduced by the pyrogallic acid, metallic silver being set free, which immediately attached itself to the sub-iodide of silver which constituted the latent image:

$$\underset{\text{Water}}{H_2O} \quad \underset{\textit{and}}{+} \quad \underset{\text{Pyrogallic Acid}}{C_6H_3(HO)_3} \quad \underset{\textit{and}}{+} \quad \underset{\text{Silver Nitrate}}{2AgNO_3} \quad \underset{\textit{produce}}{=} \quad \underset{\text{Silver}}{Ag_2} \quad \underset{\textit{and}}{+}$$
$$\underset{\text{Nitric Acid}}{2HNO_3} \quad \underset{\textit{and}}{+} \quad \underset{\text{Oxidized Pyro.}}{[C_6H_3(HO)_3+O]}$$

The precise chemical nature of the compound resulting from the oxidation of the pyrogallic acid is not certainly known. It is of a dark color, and is possibly allied to ulmic or humic acids.

Development of Wet-Collodion Plates with Ferrous Sulphate.—Ferrous sulphate (formerly called protosulphate of iron) was introduced as a developer by Robert Hunt in 1844, for calotype pictures. It was also found to answer extremely well for collodion work, and was generally known as the "iron developer." It was usually mixed in the proportion of 20 grains of ferrous sulphate, and 20 minims of acetic acid, with one ounce of water. The wet-collodion plate had a solution of silver nitrate clinging to its surface.

When such a developer was poured upon the exposed plate, the following chemical reaction first took place:

$$\underset{\text{Silver Nitrate}}{6AgNO_3} \quad \underset{\textit{and}}{+} \quad \underset{\text{Ferrous Sulphate}}{6FeSO_4} \quad \underset{\textit{produce}}{=} \quad \underset{\text{Silver}}{3Ag_2} \quad \underset{\textit{and}}{+} \quad \underset{\text{Ferric Sulphate}}{2Fe_2(SO_4)_3}$$

$$\underset{\textit{and}}{+} \quad \underset{\text{Ferric Nitrate.}}{Fe_2(NO_3)_6}$$

The nascent metallic silver is attracted, as rapidly as it is produced (the acetic acid prevents it being produced *too* rapidly), by the sub-iodide of silver which constitutes the latent image. This attraction is of a *physical* nature; and so, although the silver is liberated by a chemical reaction, yet the actual process of development belongs to the physical class of phenomena.

Chemical and Physical Restrainers.—The addition of an acid to the developers we have described slows their action considerably. Inorganic acids, as nitric or sulphuric, act too powerfully; and of the organic acids, acetic acid seems to accomplish its task with the greatest regularity. It is probable that the acid forms a molecular combination with the silver salt which has *not* been acted upon by light; and this compound does *not* attract silver, which is thus deposited upon the latent image only.

But if we *thicken* the developer, as by using some colloid substance, such as gelatine, we restrain the movement of the silver molecules, and again we give time for the silver sub-salt (which constitutes the latent image) to exercise its superior power of attraction. Thus by adding glycerine (or a strong solution of gelatine) to the developer the acetic acid my be dispensed with. The latter is a *chemical*, the two former are *physical* restrainers. A developer on this principle was recommended by Mr. Carey Lea in 1875,* under the title of the "ferro-gelatine," "collo," or "glycocoll" developer.

Physical Development Acts Externally.—All the methods of development which we have so far described may be called *physical* methods. Molecules, either of mercury (in the daguerreotype process) or of silver (calotype, collodion, etc., processes), are brought into contact with a sensitive surface upon which a latent image has been produced by the action of light. The metallic molecules attach themselves to, or deposit themselves upon, the latent image in proportion to the intensity of that image.† The action is of the nature of crystalline growth; and reminds one strongly of the methods of electro-deposition by which gilding or plating is performed. The supply of silver comes from the silver nitrate with which the plate is bathed, and not from the silver iodide *in* the film. With an ordinary wet-collodion plate this can be proved by washing the exposed plate in distilled water before applying the ordinary developing solution; it will then be found impossible to develop an image of any density; but by pouring off the developer and adding to it a silver nitrate solution, a satisfactory image will at once grow up when the developer is once more poured upon the plate. Or the latent image can be developed in *mercury* if the exposed and washed plate be treated with a solution of pyrogallic acid and mercurous nitrate. (Carey Lea.)

The ridges formed by the deposit of silver can actually be *seen* upon a developed wet-collodion plate; and they visibly obstruct the flow of developer when it is repeatedly poured over the surface of the plate. Moreover, the developed image can be destroyed by bathing the plate in dilute nitric acid, which attacks and dissolves the metallic silver at the surface.

Thus physical development is a process which acts from the *outside*, piling up an image which is raised *above* the surface of the film.

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* See *British Journal of Photography* for 13th of August, 1875.

† The varying intensity of the latent image being in turn due to the varying intensity of the light by which it was produced.

CHAPTER XX.

THE CHEMISTRY OF ALKALINE DEVELOPMENT.

Of the thousands who daily mix their pyro, ammonia, and bromide for use in development, how many, we wonder, give a thought to the "fathers of photography" who racked their brains to discover for us a wonder-working liquid, the application of which to a dry-plate should evolve with force and rapidity the picture drawn upon the plate by the lens?

Looking back for the origin of alkaline development, there is no doubt but that the *idea* was due to H. T. Anthony, of New York; and that it was extended by Leahy, of Dublin; Glover, of Liverpool; and (above all) by Major Russell.

The *Photographic News* for August 8, 1862, contains a letter from Mr. F. F. Thompson, of 2 Wall Street, New York, in which he writes: "The problem of instantaneous dry-plates is about solved by H. T. Anthony, Esq., of this city. His discovery consists in subjecting a tannin dry-plate to the fumes of weak ammonia for a few seconds, and exposing it within one day after fuming. These plates are extremely sensitive, two seconds' exposure being sufficient with small diaphragm, and instantaneous with full opening of Harrison's stereo portrait lens. The development is conducted cold in the ordinary manner."

It is probable that Mr. Anthony was induced to try the effect of ammonia fuming upon collodion dry-plates by the success which had attended his plan of treating albumenized silvered paper in the same way; a plan which it appears he practised as early as 1860.*

Another American worker, Mr. E. Borda, published certain experiments on rapid dry-plates in the *American Journal of Photography* for 1862.†

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* See letter by Col. Sellers in *British Journal of Photography* for January 1, 1863.

† Referred to by Col. Sellers in *British Journal* for August 15, 1862.

He states that having tried the plan of fuming tannin dry-plates before exposure as suggested to him by Mr. H. T. Anthony, he had gone further, and found that fuming *after* exposure, but before development, answered equally well.

The first British experimenter to repeat Anthony's and Borda's experiments was John Glover, of Liverpool, whose article on "The Dry Development of Dry-Plates" appeared in the *British Journal of Photography*, for October 1, 1862. The method was carried a step further by T. M. Leahy, of Dublin, who—writing in the *Photographic News*, for November 7, 1862—says: "In some experiments with the honey and tannin process in which I tried fuming with ammonia as an accelerator, I remarked that, when the plate was washed after the fuming, the image came out very distinctly; it struck me that the ammoniacal vapor might have become, in some manner, fixed on the plate, and that, on the application of the washing-water, it dissolved and acted as a developer. Following up this idea, I gave a plate a very short exposure in the camera, and *immersed* it in a very weak solution of ammonia; almost immediately the picture began to appear, and continued to come out until nearly all the details were visible. I then washed it well and applied the pyrogallic acid and silver, which rapidly completed the development of the picture, without the least sign of fogging or stain of any kind.

"This development of the latent image could not have resulted from any free nitrate being left in the film, as I not only wash it thoroughly after sensitizing, but also pour a 3-grain solution of chloride of sodium two or three times over it, when I again wash and pour on the tannin and honey solution. The use of the ammonia in the liquid form, I think, has one great advantage over the fuming, it acts equally, and the picture being washed before applying the pyrogallic acid and silver, no deposit (such as sometimes occurs when the *fuming* is carried to any extent) can take place."

Step by step the method of alkaline development advanced: Anthony uses the fumes of ammonia; Leahy applies the same alkali dissolved in water. But it was reserved for Major Russell to perfect the method. In the *British Journal of Photog-*

raphy, for 15th of November, 1862, Russell writes: "Having read the accounts from America of fuming dry-plates with ammonia, I next set about examining the capabilities of this agent, and during the last six weeks have made a great number of experiments with, to say the least, very promising results. . . . . Thinking that the developing action of the fumes of ammonia must be due to their action on the tannin, the first thing I did was to try the effect of mixing a small quantity of ammonia with a solution of pyrogallic acid, which is much more unstable. The liquid showed no immediate effect, but changed color slowly in much the same manner as if nitrate of silver and acid had been added. On mixing the pyrogallic acid and ammonia, and immediately pouring it on an exposed plate, its developing action is very energetic, not only bringing out the image after very short exposure, but even in some cases producing a considerable although insufficient amount of intensity, which can very easily be increased to any extent by redeveloping* with pyrogallic acid and silver. Ammonia will develop a picture by its action on tannin if the exposure has been long enough; but it must be much longer than is required when pyrogallic acid is used in the same way.

"The principal precautions necessary are: 1st. That too much ammonia be not used; one drop of the strongest solution usually sold in four ounces of water generally seems to be sufficient, with a few drops of strong alcoholic solution of pyrogallic acid added to the portion to be used. There appears to be considerable latitude in the proportion of ammonia; but if too much is used the liquid becomes strongly colored very quickly, the high lights start out at once with some intensity, but the other portions of the plate show nothing but brown discoloration. 2d. That the alkaline and acid developments be kept quite separate, the plate being thoroughly washed under a stream of water after the former. If this is neglected the picture will be entirely spoiled.

"When these precautions are observed this method appears to be easy and certain, and the picture is very bright, clear, and free from loose deposit, much more so than when the ordinary plan is adopted with an under-exposed plate. The image is entirely in the film, and shows little or no dullness of surface on any part, even when the exposure has been as short as possible to produce a tolerable picture.

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* We should now say "intensifying."—W. J. H.

"These facts appear to throw doubt on the correctness of some of the commonly received opinions as to the nature of the developing action. The effect does not depend on the presence of nitrate of silver, for pyrogallic acid and ammonia will succeed on a plate which has been immersed for some time in a very strong solution of salt, after the latter has been removed by copious washing and long soaking.

"It is hardly safe to venture an opinion as to the theory of the matter in the present state of our knowledge, but it seems to me that the decomposition of pyrogallic acid darkens the bromide or other insoluble salts of silver which are in contact with the impressed iodide. If this be so, it may account for the strongly accelerating effect of bromide (of silver) on dry-plates without nitrate, when used in a much larger proportion than would be advantageous on wet-plates from which the nitrate is removed."

One more step! Russell *mixes the ammonia with the pyro*, and finds the mixture brings out an image capitally.

A year later, Major Russell describes* the development of bromised collodion plates with a solution of carbonate of ammonia and pyro. With bicarbonate of soda and pyro the plate was quickly fogged.

It was seen that the new method of alkaline development was very promising; but it was soon found to be most successful with plates containing *bromide* of silver. The developer consisting of pyrogallic acid plus an alkali was, however, very frequently found to *fog* the plates. It was again reserved for Russell to discover † that the remedy for this fogging was the addition of a soluble bromide. He writes:

"The most advantageous way of doing this seems to be to moisten the film just before developing with a weak solution of bromide, or to mix a little of the solution with the alkaline developer, it does not much matter which, provided a suitable quantity of bromide is used in either case."

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* *British Journal of Photography* for January 1, 1863.

† *British Journal of Photography*, for 15th June and 1st July, 1884.

Major Russell was (very properly) proud of this discovery, which removed a great difficulty from the path of the early experimenters with alkaline development. Twenty-three years later he wrote in the "British Journal Almanac"* an article on "How the Restraining Action of Bromide was Discovered." This article is very short, and we may quote it in full, as a tribute to the man who first put together the three ingredients of our alkaline developer:

"On finding out that great sensitiveness could be obtained on dry-plates prepared with bromide of silver in collodion, and experimenting with a view to discover the conditions most favorable to sensitiveness, at first it seemed as if the more washed the film the more sensitive. The plan was then tried of leaving the plates, after sensitizing, to soak in water for twenty-four hours.

"The plates thus treated, to my surprise, always fogged badly. On consideration, it seemed plain enough that the fogging must be caused by the too complete removal from the film of soluble bromide which had escaped decomposition by the nitrate bath.

"A few trials showed that this was so, and that soluble bromide is a restrainer for bromide of silver, treated with an alkaline developer."

The "dry-plates" referred to in these experiments of 1862–3 were prepared by giving the plate a coating of collodion containing either a soluble bromide plus an iodide, or a soluble bromide alone. Such plates were sensitized by immersion in a bath of silver nitrate, the result being the formation of silver bromide (or silver bromide plus silver iodide) in the film. They were then *washed* (to remove the excess of silver nitrate), flowed over with a solution of tannin, and finally dried.

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* For 1887, page 240.

CHAPTER XXI.

CHEMISTRY OF DEVELOPMENT.—(III.) BROMIDE OF SILVER IN GELATINE.

The First Gelatine Emulsion Dry-Plates Developed by Maddox in 1871.—When Dr. Maddox introduced the now universally practised gelatine dry-plate process in 1871,* he found that he was able to develop an image upon them with pyrogallic acid alone, using a solution of 4 grains of pyro to the ounce of water. And this leads us to notice that it is the pyrogallic acid which is the real or principal ingredient in the developer. Pyro can develop an image by itself; the ammonia serves merely as an accelerator, and the bromide as a restrainer.

Maddox developed a thin picture with pyro alone; and then washed the plates and intensified them with silver. He attempted to use ammonia with the pyro, but the plates then fogged. He apparently did not think of the necessity for using a bromide in addition, as recommended by Russell.

Which is the Best Developer?—The first gelatine emulsion dry-plates ever sold commercially were made by J. Burgess, of London, in 1873; they were developed with "alkaline pyro"; and the same developer was recommended by Mr. Kenneth (also of London), who strove hard to introduce similar plates into general use between 1874 and 1877.

Thanks to the discoveries of Bennett, Mansfield, and others in 1878–9, as to the wonderful rapidity to be obtained in the gelatine emulsion by the use of *heat* in its preparation, gelatine dry-plates came fairly to the front in 1879, and they ousted collodion from the supremacy which it had enjoyed for nearly thirty years.

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* *British Journal of Photography* for September 8, 1871.

During the early years of the dry-plate era—1879–85, while the ordinary alkaline developer (consisting of pyro with ammonia and a bromide) was in great favor in England, workers on the Continent preferred ferrous oxalate; while in America one of the fixed alkalies—either carbonate of soda or carbonate of potash—was preferred to ammonia. During recent years, however, the claims of pyro over ferrous oxalate have been very generally admitted. With plates of inferior quality (and the dry-plates made on the Continent were certainly not equal to English plates) ferrous oxalate gives a brighter picture, but it does not permit the latitude of exposure which is the most valued feature of pyrogallic acid.

But other developers have risen up to dispute the field with pyro. First we had hydroquinone, then eikonogen, and lastly para-amidophenol. Their chemical action in the developer is similar to that of pyro. But it is to be doubted if any one of them is quite so good for all-round work as pyro. We once (perhaps rather rashly) made the assertion that "the man who is to discover a better developer than pyro-ammonia is not born yet"—but nothing has been done so far to disprove this statement.

Chemistry of the Development of Gelatine Dry-Plates.—The sensitive surface of the gelatine dry plates, or films, of which millions are now used annually, consists of molecules of silver bromide embedded in gelatine. When dry, the coating of "gelatino-bromide of silver" forms an extremely thin layer, adhering to the glass or celluloid; but when wetted by the developer the gelatine swells up and forms a layer about the one-thirtieth of an inch in thickness. When exposed within the camera a latent image is formed upon the *surface* of the film; and for our present purpose we will consider this invisible image as consisting of silver sub-bromide, Ag_2Br.

The object of the developer is to strengthen this latent image so as to render it visible, and to convert it into metallic silver.

Several developers are used for this purpose, and we will consider their chemical action in turn.

Alkaline Development with Pyrogallic Acid.—As a standard developer for our ordinary plates or films we may take the following formula:

Pyrogallic acid	2 grains
Ammonia (.880)	2 minims
Potassium bromide	1 grain
Boiled distilled water	1 ounce

When such a developer is poured upon the surface of a gelatine plate which has been exposed within the camera the following chemical changes take place:

$2Ag_2Br$	+	$C_6H_3(HO)_3$	+	$2NH_4HO$	=	$2Ag_2$	+
Silver Sub-bromide	*and*	Pyrogallol	*and*	Ammonia	*produce*	Silver	*and*

$2NH_4Br$	+	$[C_6H_3(HO)_3 + O]$	+	H_2O
Ammonium Bromide	*and*	Oxidized Pyro	*and*	Water.

The ammonia probably forms a combination with the pyrogallic acid (or pyrogallol, as it is more properly termed) which may be designated ammonium pyrogallate. This substance attacks the silver sub-bromide but *not* the silver bromide. The result is that the bromine in the silver sub-bromide is abstracted, and metallic silver is produced. This takes place, be it remembered, on the *surface* of the film only.

But the nascent silver has a powerful chemical action upon the layer of silver bromide *underneath* the surface layer of sub-bromide. It combines with this bromide and reduces it to the state of sub-bromide:

Ag	+	$AgBr$	=	Ag_2Br
Silver	*and*	Silver Bromide	*produce*	Silver Sub-bromide.

Use of Soluble Bromides as Restrainers.—It is usually found necessary to add a small quantity of either potassium bromide or ammonium bromide to the alkaline pyrogallic developer. Different makes of dry-plates differ much as to the quantity of

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NOTE.—Another view of the phenomena of development was suggested to me by the well-known fact that the presence of water is indispensable. If we suppose the first chemical action that takes place to be the decomposition of the water, $H_2O = H_2 + O$, then the pyrogallic acid will be oxidized by the oxygen, while the hydrogen will combine with the bromine of the sub-bromide to form hydrobromic acid, $H + Ag_2Br = HBr + Ag_2$. W. J. H.

bromide which they require; but the maker's formula usually gives the proper proportion.

When the exposure has been very short, and a weak developer is employed, it is possible to dispense with such a "restrainer" altogether.

Many workers who take care to use only the best brands of dry-plates invariably dispense with bromide for their instantaneous pictures.

The office of the bromide—and we may say at once that we prefer *potassium* bromide—is to prevent the reduction of silver upon those parts of the plate which have not been affected by light; to save the plate from being "fogged," in fact.

Now silver bromide is soluble in a solution of potassium bromide, a fact which shows that the two substances have some chemical affinity for one another. It is probable that the one bromide forms a loose molecular combination (= double salt) with the other:

KBr	$+$	$AgBr$	$=$	$KBrAgBr$
Potassium Bromide	*and*	Silver Bromide	*produce*	Double Bromide of Potassium and Silver.

The double bromide is better able to resist the action of the developing solution than the silver bromide alone; and thus the unexposed parts of the plate are kept clear from fog.

Ferrous Oxalate as a Developer.—The use of ferrous oxalate as a developer was discovered almost simultaneously by Mr. Carey Lea in America, and by Mr. W. Willis, Jr., in the year 1877.* It is generally prepared by making saturated solutions of potassium oxalate and of ferrous sulphate, and then pouring (not more than) one part of the latter into three parts of the former. Chemical action at once takes place, and the color of the mixture should be a clear ruby.

Before mixing the solutions it is well to add a few drops of sulphuric acid (3 or 4 to each ounce of the liquid) to the fer-

$FeSO_4$	$+$	$2K_2C_2O_4$	$=$	$K_2Fe(C_2O_4)_2$	$+$	K_2SO_4
Ferrous Sulphate	*and*	Potassium Oxalate	*produce*	Potassio-Ferrous Oxalate	*and*	Potassium Sulphate.

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* *British Journal of Photography* for 1877, p. 293.

rous sulphate solution. About the same quantity of a 10 per cent. solution of potassium bromide should be added to the mixed developer to act as a restrainer.

The above proportions (1 to 3) are the strongest permissible; but it is better to use 1 to 4; and for lantern slides and bromide paper (for which ferrous oxalate is an admirable developer) it should be used weaker still, say one 1 to 6.

When a solution of ferrous oxalate is poured upon an exposed dry-plate, the following reaction takes place:

$6FeC_2O_4$	+	$3K_2C_2O_4$	+	$6Ag_2Br$	=	$6Ag_2$	+	$6KBr$	+	$3Fe_3(C_2O_4)_3$
Ferrous Oxalate	*and*	Potassium Oxalate	*and*	Silver Sub-bromide	*produce*	Silver	*and*	Potassium Bromide	*and*	Ferric Oxalate.

Ferrous oxalate is a developer which gives particularly clear and brilliant negatives, and if the exposure has been correct, or very nearly so, it is all that can be desired; it has not, however, nearly the "latitude" of pyro.

Under-exposure may be met—to some extent—by adding to each ounce of the developer from five to ten drops of a 5 per cent. solution of "hypo"; this has a marked effect in bringing out detail.*

The chemical effect of the "hypo" is to remove from the developing solution, or rather to convert into comparatively harmless substances, the ferric oxalate and the potassium bromide formed during development, both of which are powerful restrainers. The ferric oxalate is acted upon by the hypo as follows:

$Fe_2(C_2O_4)_3$	+	$2Na_2S_2O_3$	=	$Na_2S_4O_6$	+	$Na_2C_2O_4$
Ferric Oxalate	*and*	Sodium Thiosulphate	*produce*	Sodium Tetrathionate	*and*	Sodium Oxalate
					+	$2FeC_2O_4$
					and	Ferrous Oxalate.

The potassium bromide is also converted into sodium bromide, whose restraining action is less energetic.

$Na_2S_2O_3$	+	$2KBr$	=	$K_2S_2O_3$	+	$2NaBr$
Sodium Thiosulphate	*and*	Potassium Bromide	*produce*	Potassium Thiosulphate	*and*	Sodium Bromide.

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* Abney, in *Photographic Journal* for 1880; pp. 22, 160.

CHAPTER XXII.

CHEMISTRY OF ALKALINE DEVELOPMENT (CONCLUDED).

Alkaline Development Acts Internally.—We have seen that in the "acid" development of wet-collodion plates, etc., the silver iodide in the film merely served as a foundation on which to form the latent image. That image was subsequently strengthened, built-up, or "developed" by depositing silver upon it from a developing solution (containing nitrate of silver, plus a reducer, plus an acid) which was poured upon its surface. The deposit of silver forming the picture thus *grows upwards* from the surface of the plate, and is composed of matter which the sensitive surface did not originally contain.

In alkaline development exactly the opposite takes place. The image grows *downwards*, and is fed and added to by silver *already contained in the film.*

Our gelatine dry-plates and films are coated with gelatine containing bromide of silver (= gelatino-bromide of silver emulsion). Light forms a "latent image" on the surface, which image consists—for chemical purposes we may say—practically of silver sub-bromide, Ag_2Br.

The alkaline developer with which the plate is bathed separates these two elements, combining with the bromine and liberating the silver:

$$Ag_2Br \quad = \quad Ag_2 \quad + \quad Br$$

Silver sub-bromide *produces* Silver *and* Bromine.

Now when an element is set free—as the silver is in this case—atom by atom, it is, chemically, in a peculiarly active condition (known to chemists as the "nascent" state).

This nascent silver immediately attacks the molecules of silver bromide which form a layer *underneath* the layer of silver sub-bromide which composes the latent image. It combines with this silver bromide, reducing it to the state of sub-bromide:

$AgBr$	$+$	Ag	$=$	Ag_2Br
Silver Bromide	*and*	Nascent Silver	*produce*	Silver Sub-bromide.

The layer of sub-bromide so formed is in its turn attacked by the developer, and nascent silver is again liberated. And so the action goes on until it passes downwards right through the thickness of the film and reaches the glass or celluloid at the back. The developed image can then be seen by looking at the *back* of the plate; and it consists of dark-colored reduced silver.

The coating of gelatine emulsion may be put on the plate so heavily that it is quite a quarter of an inch thick when swollen by soaking, and it may be so highly charged with silver bromide as to be quite opaque. Notwithstanding this, it will be found easy to develop an image right through to the glass support or backing. In this case the silver molecules at the back could not have been affected by *light*, and their conversion to metallic silver can only be explained by the downward growth of the image, due to the chemical action of the developer.

From the same cause the image also spreads *laterally* or sideways. Microscopic examination of a film proves this clearly; and in photomicrography it is sufficient to interfere with the absolute sharpness which is desirable.

Abney's Experiment.—A remarkable experiment, due to Captain Abney, is to expose a gelatine dry-plate in a camera (so producing a latent image), and then to coat one-half of it with collodio-bromide emulsion (bromide of silver emulsified in collodion). The plate is then developed as usual, when it is found that the image on the coated half becomes much more dense than that on the uncoated part. If the film of collodio-bromide be then stripped away from the gelatine beneath, it will be found *that there is an image on each.* The image has *grown upwards* through the collodio-bromide (which was not exposed to light at all), as well as downwards through the gelatine emulsion. Starting from the surface of the gelatine film, the image has been fed with silver both from above and from below.

This strongly reminds us of the electrolytic deposition of metals, as in electro-plating; and the attraction by which each atom of deposited silver draws to itself other atoms of the same metal is beyond question of a "polar" nature, and almost certainly electrical.

Relation of Development to Rapidity.—The rapidity of our modern gelatine dry-plates is not altogether due to the superior sensitiveness to light of the emulsion of gelatino-bromide of silver with which the plates are coated; it is also in no small part owing to the fact that we are able with such plates to use a much more powerful developer. In the old wet-collodion, etc., processes the plate was covered during development with a solution of silver nitrate. Now if an alkaline developer be applied to a plate upon or in the film of which there is free silver nitrate, a deposit of metallic silver is produced all over the plate, which is then said to be "fogged." In such processes an *acid* developer was necessarily employed; but acid developers are not nearly so powerful as alkaline developers. Again, in our modern dry-plates the particles of silver bromide are individually embedded in gelatine, and this gelatine acts as a physical restrainer. A developer which is so strong as to be able to reduce silver bromide when applied to that substance separately, cannot affect it when the silver salt is emulsified in gelatine. The gelatine wraps round and encloses each tiny particle of the silver bromide, and causes the chemical action of any developer to be slow and steady. This gives time for other forces, as electricity, to play their part.

Owing to the numerous developers now employed, and to the fact of a somewhat general similarity of appearance between them (especially when made up as solutions), it is often useful to know how to distinguish them from one another. The following table* affords the means of doing this:

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* By L. Van Neck, in the *Bulletin Belge*, 1890.

REACTIONS OF VARIOUS DEVELOPERS.

	HYDROQUINONE (Dr. Byck's Yellowish Cryst.)	PYROGALLOL. (White Sublimate.)	PYROCATECHIN. (Grayish.)	HYDROQUINONE. (White Needles.)	FIKONOGEN. (Yellowish Crystal.)	RESORCINE. (Sublimed.)	HYDROXYLAMINE HYDROCHLORATE. (White Cryst.)
TASTE	Sweet, slightly bitter	Slightly bitter	Bitter	Sweet, slightly bitter.	Saline	Sweet	Acid.
SOLUTION	Colorless	Colorless, becoming brown.	Colorless, becoming greenish.	Colorless, becoming slightly brownish.	Colorless, rapidly turning dark-brown.	Colorless	Colorless.
REACTION	Neutral	Acid	Acid	Neutral	Neutral	Neutral	Very acid.
ACTION OF HEAT.	Fusible and volatile.	Fusible and volatile.	Fusible and volatile, 240 deg. C.	Fusible and volatile.	Fixed residue, carbonizes and becomes incandescent, leaving a white saline residue.	Fusible and volatile.	Fusible and volatile.
SOLUTION OF FERROUS SULPHATE.	Nil	Blue coloration	Nil. turns green after long standing.	Nil	Violet coloration	Nil	Nil.
SOLUTION OF FERRIC CHLORIDE.	Nil	Dark-brown coloration becoming violet with excess of sodium carb.	Emerald green, becoming violet with little sod. carb. and red with excess.	Nil	Yellowish-green, becoming rapidly yellowish-brown, and then dirty brown with sod. carb.	Violet blue	Nil. decolorizing the ferric chloride.
TINCTURE OF IODINE.	Decolorizes the tincture.	Red-brown coloration.	Nil	Decolorization	Reddish-brown coloration.	Instantaneous decolorization.	Decolorization.
SOLUTION OF PLUMBIC ACETATE.	Nil	White precipitate.	White precipitate	Nil	White precipitate, turning black.	Nil	At first nothing; then a precipitate forms.
SOLUTION OF POTASSIUM CARB.	Yellowish coloration, turning brown in air.	Yellow, turning blackish-brown.	Yellow becoming brown.	Yellow, turning brown rapidly.	Yellow, turning brown rapidly on shaking.	Nil	Nil.
SOLUTION OF SILVER NITRATE.	After a time a gray precipitate, solution colorless.	Slow reduction to metal, solution brown.	Very slow reduction, solution yellowish.	Slow reduction	Instantaneous reduction.	Nil	Whiteprecipitate.
DILUTE HYDROCHLORIC ACID.	Nil	Nil	Violet coloration	Nil	Rose coloration in diluted solution, becoming greenish on addition of ammonia.	Nil	Nil.

THESE REACTIONS TAKE PLACE IN A ½ % SOLUTION OF DEVELOPING AGENT.

CHAPTER XXIII.

ORTHOCHROMATIC PHOTOGRAPHY.

DIFFERENCE BETWEEN THE OPTICAL AND THE CHEMICAL EFFECTS OF LIGHT.

What is light? It is not a *thing;* it is not any kind of matter, for it has no weight. And yet light and matter are inseparable. Light is one of the physical forces—it is grouped with heat, sound, gravity, electricity, etc.—and is consequently a state or affection of matter.

Two centuries back the mighty Newton argued that light *was* matter; maintaining in his "Corpuscular Theory" that all light-giving bodies continually emitted infinite numbers of tiny particles or "corpuscles," which travelled through space; and that our sense of sight was due to the striking of some of these corpuscles upon the retina or sensitive expansion of the optic nerve which lines the back of the eye-ball.

But Newton's corpuscular or emission theory of light—though long upheld by his great name—has been disproved by the researches of Huyghens, Young, etc., who discovered that light is due to the rapid motion of the molecules of self-luminous bodies; this motion producing waves in a medium called the ether, which is believed to fill all space. The ether is a gaseous substance of almost infinite tenuity—we should have to weigh it by the cubic mile to find that it had any weight at all—and it fills the universe, occupying all the space between the earth and the sun, moon and stars. It is able to pass through even solid bodies with the greatest ease; indeed, Sir W. R. Grove remarks that "the ether passes through the earth as easily as the wind through a forest of trees."

The waves produced in this ether by luminous bodies pass through it with the almost inconceivable velocity of 186,000 miles per second; and, when they strike upon the retina of the eye, they set the fibres of the optic nerve in motion, and this produces in the brain the sensation of light. This wave motion can be imitated by throwing a stone into the middle of a pond. Waves are produced which spread in circles until they reach the margin. The light-waves from the sun take rather more than eight minutes to reach the earth; but the nearest fixed star is at such an enormous distance that an undulation or wave of light leaving that star, for example, on the 1st of January, 1893, would not reach us until the end of June, 1896.

Let us conceive of light, then, as a kind of motion; and compare the waves of ether falling upon the substance of our earth, with the waves of water which we know are able to produce such tremendous effects upon our coasts. The waves of light do their work more quietly than the waves of water, but their action is none the less real, and of far greater importance. If our eyes were able to distinguish these waves of light, and also the molecules of silver salts with which our dry-plates are coated, we should see the ether dashing upon the molecules and breaking them to pieces, just as we may see the mighty water waves of the Atlantic battering beach and cliff in a spring storm.

Mathematically and by experiment it has been demonstrated that the undulatory or wave theory of light is the true one.

In the study of light (which is called optics) we call the direction of the line along which the light-wave passes, a *ray* of light.

COMPOUND NATURE OF WHITE LIGHT.

When a ray of sunlight is caused to pass through a three-cornered piece of glass known as a prism (of which the "drops" of lustres, some chandeliers, etc., are examples) it is found to be spread out (on the other side where it emerges from the prism) into a band of colored light. This colored band really consists of an infinite variety of colors, but it is usual to distinguish seven principal colors—red, orange, yellow, green, blue, indigo and violet. The word "roygbiv" will prove an *aide memoire* for these colors, as it gives the first letter of the name of each color in its proper order of succession. Thus the prism shows white light to be a compound of all the colors of the rainbow, the latter natural phenomenon being indeed produced by the passage and consequent decomposition of (white) sunlight through minute prisms of ice or drops of rain high up in the air.

The *cause* of the decomposition of a ray of white light into a colored band by passage through a prism is that the light is, in the first place, bent or *refracted* by passing from the air to the glass on entering the prism, and still more bent (in the same direction) where it emerges from the prism. But the second and main reason is that the variously colored parts of the ray are not refracted equally, the red rays being bent the least and the violet rays the most. The former are known as the *less* and the latter as the *more* refrangible rays; and the entire band of colored light is called the *spectrum*. The spectrum of sunlight is crossed by a number of vertical black lines (called Fraunhofer lines, after the German optician who first mapped them in 1814). These lines are due to the presence of certain elements in a vaporous state in the atmosphere of the sun, and they are not seen in the spectrum of the electric light or of the lime-light, etc.

The Fraunhofer lines serve usefully as an *index* to the various parts of the spectrum, as they never change their position. The principal lines are indicated by the letters of the alphabet; *A* is at the extreme end and *B* in the middle of the red; *C* separates the red from the orange; *D* is in the yellow, *E* in the green, *F* in the blue, *G* in the indigo, and *H* in the violet.

An instrument specially constructed to study the spectra of bodies is called a *spectroscope*. It consists of a narrow slit through which light is admitted; a lens or lenses to render the rays parallel; a prism or prisms to decompose the white light; and a small telescope through which the spectrum so produced can be examined.

Every one who has watched water-waves—either from the deck of a vessel or from a beach—must have noticed that sometimes the highest parts or crests of the waves are close together, while sometimes they are far apart. The length of a wave is measured in a straight line from crest to crest. Sometimes this is only a foot or two, but it may be some hundreds of times greater. The wave-lengths of light are almost inconceivably short, but they have been accurately measured, and the results as expressed in "tenth-metrets" or ten-millionths of a millimetre* are

A = 7604
B = 6867
C = 6562
D = 5892
E = 5269
F = 4861
G = 4307
H = 3968

Beyond the red there are rays—the "infra-red rays"—which are invisible to our eyes, but which have much heating power, strongly affecting the thermometer. These have been mapped as far as wave-length 10,000 by Abney, and they have been detected down to wave-length 22,000. Beyond the violet there are other invisible rays—the "ultra-violet"—which have a powerful chemical action; these have been traced as far as wave-length 2,000 by Hartley.

Centres of Heat, of Light, and of Chemical Action in the Spectrum.

Every part of the spectrum is capable of producing heat, light, and chemical action. As to the two former, no doubt the point of greatest heat lies in the "infra-red," and is therefore produced by rays which are incapable of affecting the retina. The point of maximum luminosity or brilliancy is in the yellow-green. But the chemical action of the differently-colored rays depends largely on the substance which is chosen to receive them. For the sensitive salt—ordinary silver bromide—which is generally used on our dry-plates, the blue rays are the most powerful.

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*The millimetre = .03937 inches, or the twenty-fifth part of an inch nearly.

The three curves shown in figure 1 represent, by the height of each curve above the base line, the powers of heat, of light, and of the chemical force possessed by each part of the spectrum.

With the heat rays we are but little concerned in photography; we do not secure our pictures by their aid, but by the aid of the rays of light.

At first sight it may seem fortunate that those parts of the spectrum (the yellow, green, and red rays), which can exert but little chemical force, are those which are most luminous, producing the greatest effect upon our eyes; while the blue and violet rays, which really do the work of "taking pictures" on our dry-plates, are comparatively dark as seen by the eye. This enables us to take our photographs by the aid of the blue and violet rays, and then to develop them in a room lighted by the yellow or red rays.

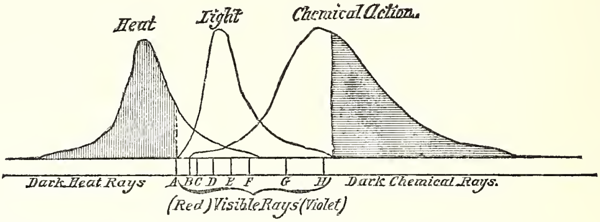

FIG. 1.—Diagram of the various intensities of light, heat, and chemical action throughout the spectrum.

The height of each curve above the horizontal line indicates the intensity at that point. The rays which do not affect the eye are shaded. The Fraunhofer lines are lettered from *A* to *H*.

Yet further thought will show that as a fact this state of things is most unfortunate. Photographs so taken cannot be true transcripts of natural objects. The sensitive dry-plate "sees" an aspect of nature, but it is not identical with that which is impressed upon the retina. In the resulting prints the yellows, greens, and reds come out far too dark; the blues and violets too light.

The illuminating and chemical forces respectively of the variously colored rays are shown in the following table:

Colors.	Luminous Intensities.	Chemical Intensities on Silver Bromide.	Lines.
Dark Red.............	Just perceptible.	0	A
Red....................	32	5	B
Bright Red...	94	10	C
Orange..................	640	50	D
Yellow..................	1000	100	..
Green...................	480	200	E
Blue....................	170	500	F
Indigo..................	31	1000	G
Violet..................	6	650	H
Ultra Violet............	0	450	..

Thus a light yellow, just bordering on the green, is the brightest or most luminous color; next to this come orange and green; while dark blue (indigo) and violet are the darkest colors.

But the chemical effect is shown by the table to be very different; the maximum effect is here produced by the blue end of the spectrum.

In figure 2 the chemical effects of light upon the three sensitive salts of silver—the chloride, the iodide, and the bromide—are compared, graphically, with the luminous effects of the differently colored rays. It will be seen that each of the three curves representing chemical effects differ widely from the curve of luminosity.

The question then arises—Is it possible to obtain a substance which shall "see" chemically as we see; which shall be most sensitive (like our eyes) to yellow rays, and least so to dark blue; with the other colors producing chemical effects in proportion to their luminosity. Our photographic plates would then furnish an accurate transcript—in black and white—of nature; their "tones" would be correct, as the artist says. The attempts to bring the chemical curves into coincidence with the curve of luminosity have resulted in the discovery of orthochromatic photography; and of this we shall next proceed to treat.

In the preceding paragraphs we have tried to explain how differently the many colors of which white light is composed—and which we may here for convenience sake reduce to two only, yellow and blue—affect our eyes and our dry-plates respectively. To our eyes the yellow looks bright and the blue dark, while we all know that if we photograph on an ordinary plate an Italian peasant, dressed in a blue skirt and a yellow bodice, the resulting print will show the skirt white, or nearly so, and the bodice black.

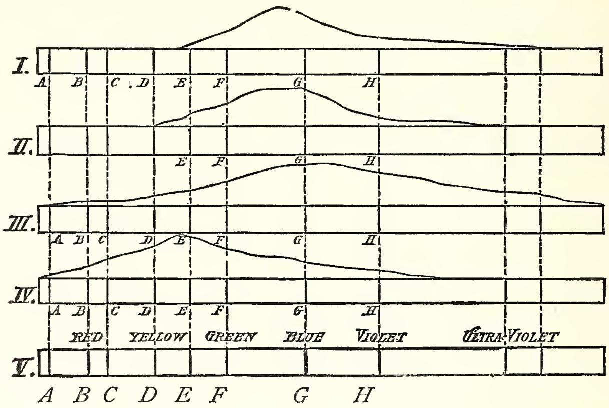

Fig. 2.—*I.*, silver chloride; *II.*, silver iodide; *III.*, silver bromide; *IV.*, luminosity of the spectrum; *V.*, Fraunhofer lines in the solar spectrum.

The height of the curve above the horizontal line in each case shows the intensity of the action at that point.

The keen eye of "Mr. Punch" noted this long ago, and in the issue for a certain week in July, 1861, we have a droll picture of a footman showing his photograph to the housemaid. "Why, Tummas," says the delighted Mary, "it's the very moral of yer!" "Pretty thing, ain't it," replies Thomas. "Pity the yaller of the uniform comes so black!"

Several eminent professional photographers have written pamphlets of instructions for their lady sitters, pointing out how the color scale is changed by photography. But sitters with auburn (to put it mildly) or golden hair, have always been a trouble to the operator, who usually resorts to powder-ing such hair plentifully as a partial remedy, while the freckles which as often as not enhance the beauty of a blonde, are reproduced as transparent spots on the negative (black on the print), giving no end of trouble to the retoucher.

Then as to copying pictures. What a parody is a copy, on an ordinary plate, of an "old master," or a harvest scene, or a sunset, or indeed any picture which depends mainly on the artist's skilful use of color for its effects.

All these defects were noted in the early days of photography—thirty or forty years ago—and sundry attempts were made to remedy, or at all events mitigate, the faults complained of.

An editorial* article in the *Photographic News* for Oct. 15, 1858, "On Copying Paintings by Means of Photography," suggests the use of the bromide of silver instead of the iodide (the latter being the salt of silver in general use at that time) and goes on to recommend the placing of a solution of sulphate of quinine in a glass cell in front of the lens. The quinine absorbs and quenches most of the violet and ultra-violet rays; whose action on the silver salt is so great, on the eye so small. Crookes adds: "A thin piece of yellow glass employed in the same way will act even more vigorously, and, were it not for the uneven surface which this kind of glass usually has, it would answer the purpose admirably." Experiments showing the effect of using as many as *five* thicknesses of yellow glass in front of the lens when photographing brilliant colors are then detailed:—"At this stage the photographic effect of the different colors was much nearer their true effect on the retina than if they had been copied in the ordinary way, but they were still very far from giving the tones which an engraving of the same subject would have presented. The too energetic action of the blue color was entirely overcome, but the red and yellow still offered difficulties which, we fear, no amount of obstruction would ever have properly overcome."

In this article the true function of the yellow screen is correctly pointed out. Its use is to subdue the blue and violet rays, reducing their too energetic action to a more manageable one. But on ordinary films the action of the remaining part of the spectrum—the greens, yellows, and reds—is so slight that the time of exposure is so much increased as to make the method, by itself, valueless. Moreover, even if sufficient time be allowed, the general effect is flat, and even foggy.

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* William Crookes, the famous chemist, then edited the *News*, and the article is presumably by him.

As far as the "uneven" character of the yellow glass is concerned, that is now obviated. For Mr. J. R. Gotz, of 19 Buckingham Street, Strand, London, has supplied us with sheets of yellow plate-glass, the twenty-fifth part of an inch in thickness, which can be had in four different depths of tint, and which answers admirably when used in conjunction with orthochromatic plates. Similar screens can now be had from several other firms.

Having found that it is useless to hope to obtain a correct tone, or "tonality," by excluding those rays (the most refrangible—blue, violet, and ultra-violet) which are most active or "actinic" in bringing about chemical changes, it remains to be seen whether it is not possible to exalt or increase the sensitiveness of the silver salts which we employ for the less refrangible rays, the yellow, green, and red.

Draper, Hunt, and many others of the early workers in photography, imagined that there were three distinct spectra laid one upon the other, as it were. The chemical or actinic spectrum they thought extended from the red to the ultraviolet rays, but it was nearly or altogether neutralized at the red end by the other overlapping spectra. At its free end (the ultra violet) its rays were capable of producing the most powerful actinic effects. Similarly the heat spectrum had its free end beyond the red; for the ultra-red rays are, we know, those which possess most heat. Lastly, the luminous spectrum occupied the centre (overlapping the others on each side) and its greatest power of luminosity lay in the yellow.

But later researches have shown that this theory is altogether incorrect, and that in examining into the powers and qualities of the various rays which constitute what we call the "spectrum" of white light, *we must consider the substance upon which the rays fall*, as well as the rays themselves.

We call the blue and violet, etc., rays "actinic" and "chemical" simply because the substances we usually employ in photography—the salts of silver—are in their normal state most readily affected by these rays. But there are other materials upon which the yellow and red rays are most effective, chemically speaking. So, also, it is a fact that the yellow rays affect our eyes most powerfully; but there are good reasons for believing that to some of the lower organisms it is the violet light which is most luminous.

The founder of orthochromatic photography is Professor Hermann W. Vogel, of Berlin. In an article which appeared in the *Photographic News* for December 12, 1873, he announced that if bromide of silver be *dyed* by means of certain yellow or red dyes, it becomes sensitive to yellow or red light. Vogel used principally dry-plates coated with an emulsion of silver bromide in collodion. The first dye he used was the substance known as "corallin," which he dissolved in alcohol and added to the collodion emulsion until its color was a "vigorous red." Plates coated with this colored emulsion were "nearly as sensitive to yellow light as to indigo." Aniline-green was also tried, which was found to sensitize for the red rays. A crucial experiment is described in this paper. "A blue band upon a yellow ground was photographed. With an ordinary iodide of silver collodion plate, I obtained a white band upon a black ground. With a bromide of silver coralline plate, upon which blue and yellow acted with equal power, nothing could be obtained; I foresaw, and for this reason I put in front of the lens a yellow glass plate, which absorbed the blue light, and allowed the yellow rays to pass through unheeded; and then I was enabled to obtain, after a sufficiently long exposure, a dark band upon a light ground."

Numerous contributions on the subject from Professor Vogel's pen appeared in the *Photographic News* during 1874–5–6 and 7. His conclusions were opposed, or doubted, by Monckhoven, Carey Lea, Spiller, and others, but his arguments were sound, his work was true, and they received valuable confirmation from Capt. Waterhouse, of Calcutta, who in 1875 photographed the green, yellow, and red rays of the spectrum (as well as the more refrangible blue and violet) by using plates stained with the pink dye called roseine, with "Judson's" dyes (including turmeric), with chlorophyll, etc.

In 1876 Waterhouse for the first time added a red dye known as *eosin* to a collodio-bromide emulsion, and with good results. Vogel's experiments were conducted mainly on the spectrum, but Waterhouse tested his eosin-collodion plates on landscapes. He writes: "From this remarkable sensibility to the green and yellow rays, it might have been anticipated that wet plates prepared with the eosin-stained collodion would show an increased sensitiveness for foliage and other colored objects of a green or yellow tint. On trying a landscape, I found that though the collodion was by no means strongly stained, the exposure was increased to about three times what was necessary for wet collodion. There was no marked increase of detail in the foliage, but, if anything, a decrease. There was, however, a great increase in the density of the image and in the clearness of the shadows. Subsequent trials, both with dry bromide and wet bromo-iodide plates, on bouquets of flowers and a stained-glass window, comprising red, green, blue, and yellow, showed that but little practical advantage was to be gained by the use of the stained collodion, though the plates were undoubtedly more sensitive to yellow than is ordinarily the case, and showed the same increase of intensity, which may be a further advantage.

"I have not yet had leisure to fully investigate the action of the dye; but this brief record of a few results obtained with it may be of interest as bringing to notice a coloring matter which in some degree supports Dr. Vogel's theory, that a film of dry bromide of silver may be rendered sensitive to certain rays of the spectrum by being stained with a color which absorbs those rays—and also as showing that the photographic action of the spectrum is but a slight index to the action of the colored objects around us."

We have quoted these paragraphs from Capt. Waterhouse's paper because he was the first to use the dye—eosin—which is the one now mainly used for orthochromatic photography; because he was the first apparently to test his color sensitized plates on landscapes; and because he so correctly points out that photographing the spectrum with its band of pure colors is one thing, while photographing the colored objects found in nature is quite another. Scarcely any colored object reflects or is visible by pure monochromatic light. The brilliant red of many flowers will be found (when examined spectroscopically) to contain a proportion of blue rays, etc. But more than this, all objects reflect—in addition to any proper color which they may possess—*a certain amount of white light*, and it is by this reflected white light that they are photographed.

Thus we do not photograph the green leaves, or grass, by their green light, but by the white light which they reflect in addition to the green. This reflection varies with the angle of each leaf, and this explains the common "spottiness" of foliage, one leaf—at the proper angle for reflecting white light into the lens—coming out quite white in the print, while its neighbor—at a different angle—is quite black.

One of the first scientists to confirm and support the discoveries of Professor Vogel was the famous French *savant*, Edward Becquerel. In the latter part of 1874 he communicated to the Paris Academy of Science the results of experiments on films stained with coralline and with aniline green, which showed an action in the yellow and green similar to that obtained by Vogel. But Becquerel went further: he used *chlorophyll*, the green coloring matter of plants, to stain a collodio-bromide emulsion. Plates coated with this emulsion and exposed to the spectrum showed an action not only in the blue and violet, but also in the green, the orange, and the red. Becquerel also noticed that the points of maximum action on the plate corresponded with the absorption lines of the chlorophyll. As to these absorption lines, we may explain that when solutions of different bodies are examined by means of transmitted light with a spectroscope, we commonly see dark bands —"absorption bands or lines"—in their spectra. These dark spaces show that the light has been there *absorbed* by the substance.

Now light is a form of energy, and we know that when one kind of energy disappears, another kind appears—for "energy is indestructible." What becomes of the lost light? It is probably converted into either heat or chemical action, or more probably into both of these forms of energy.

The first writer to make any practical use of Vogel's discovery was Ducos Duhauron, who employed* collodio-bromide containing coralline, etc., to obtain the negatives he desired to employ in his process of "Heliochromy," or printing in colors. We do not refer, except incidentally, to heliochromy in these articles, but in the appendix references to it are included. Orthochromatic photography is indispensable to heliochromy.

Duhauron in 1878 went further, and employed improved methods of a similar description.

After 1877 orthochromatic photography went to sleep for a few years. Vogel—its discoverer—had only a scientific interest in it; and the work of Waterhouse seemed to show that it had not much practical utility.

Then in 1879-80 came the great revolution—the displacement of collodion by gelatine. Seeing that gelatine dry-plates were so greatly superior to collodion in rapidity, it was natural to study their other comparative properties also. One might have imagined that the effect of dyes upon such gelatine plates—the attempt to sensitize them for the less refrangible rays—would soon have been made, but it was not so.

In February, 1882, Captain Abney used bromide paper dyed with eosine in his *Cantor Lectures* delivered before the Society of Arts.

After an interval of six years the first move came from France. On 8th January, 1883, a patent (specification No. 101) was taken out in England by C. D. Abel, "on behalf of Pierre Alphonse Attout, called Tailfer, and John Clayton" for the "application of eosine to gelatino-bromide emulsions or coated plates to get the relative lights and darks correctly in spite of varying color.

"The eosine is dissolved in ammonia,† and added to the emulsion at the moment of its formation.

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* Photographic News, June 5th, 1874.

† The other or "fixed" alkalies—as the carbonates of soda or potash—are of no use in preparing isochromatic plates. When the plates are dried they crystallize.

"Plates that are already coated and dry have the ammoniacal solution of eosine to which alcohol has been added, poured over the film. They are washed, the eosine remaining fixed.

"The term eosine is used inclusively: and other alkalies than ammonia may be used."

The same principle had been patented a few weeks earlier in France. The date given above is merely that on which the patent was "handed in"; the specification would not be *published* till at least six months later.

At first the "Attout-Tailfer" plates found but little favor in England; and it was not until a medal was awarded to them at the Inventions Exhibition, held at South Kensington, London, in 1885, that their merits began to be recognized. The English patent was soon afterwards purchased by Messrs. B. J. Edwards & Co., The Grove, Hackney, London, who advertised them as "Isochromatic" * plates. They were brought still further into notice by the work of Messrs. Dixon & Gray, who exhibited some wonderfully good copies of oil paintings at the Pall Mall Exhibition of the Photographic Society of Great Britain, held in 1886; copies which had been made upon plates prepared in a similar way to that described in Tailfer's patent. Ever since that date the use of isochromatic plates has increased in Great Britain, and for copying paintings, flowers, etc., and for the highest class of studio work they are now considered indispensable.

It will be noted that the Tailfer patent claims the use of "eosine," and this term includes a very large number of dyes, of which the variety known as "erythrosine" is that now used in the manufacture of the isochromatic plates; it also includes the use of any alkali with the dye, and this is another important point.

At about the same period (1882-6) that the Tailfer plates were being introduced into England, rumors came from time to time from Germany that the famous house of A. Braun et

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* From the Greek *isos*-equal, and *chroma*-color; not a very happy word, since our object is not to render all colors *equal* in their effect upon our dry-plates, but to cause them to produce the same *chemical* effects as they do *luminous* effects. The word "isochromatic" was suggested for the Tailfer plates in 1882 by the eminent French statesman, M. Paul Bert, at that time professor at the Sorbonne in Paris.

Cie, of Dornach and Paris, had discovered some "secret collodion process" by which they were able to obtain photographic copies of oil paintings, etc, superior to anything that had been done before. The "secret process" was, no doubt, the use of collodio-bromide dyed plates, but the firm naturally did not publish their method. In 1884 Messrs. Braun were permitted to erect a temporary studio in front of the National Gallery, London, and to copy between 300 and 400 pictures belonging to the famous collection there exhibited. The prints showed a marvellous improvement in the rendering of the reds and the yellows, and it was argued by many that such an improvement must be due to some system of elaborate retouching. But an eminent English worker was permitted to visit Dornach and examine the negatives, and he testified that the results were *not* due to retouching. Of course we now know well enough that by the combined use of "eosine" and a yellow screen similar results are easy of attainment, but the general incredulity on this point which prevailed so recently as 1886, when Mr. Bird read his paper before the Photographic Society of Great Britain, shows the rapid advance which has since been made.

After the general recognition of the immense value of color-sensitized plates (at all events for special purposes) in 1885-6, Dr. Vogel probably saw what a mistake he had made in not at once adapting his process—originally introduced for collodion in 1873—to gelatine dry-plates. For one thing, Tailfer had not attempted to take out a patent in Germany, so the matter had perhaps not been borne in upon the learned Doctor's inner consciousness as it otherwise might have been.

The English patent of "Dr. Hermann Wilhelm Vogel, of 124 Kurfursten Strasse, Berlin, Chemist," is dated 29th November, 1886, and is for "An improved process for manufacturing isochromatic emulsion plates highly sensitive to light." The preamble states that "In the year 1873 I made the discovery that chloride and bromide of silver, which are only sensitive to violet, indigo, and the blue light of the spectrum, can be made sensitive to green, yellow and red rays by mixing the above-mentioned salts with bodies that absorb the latter rays. If, for instance, chloride or bromide of silver is mixed with aniline red, which absorbs yellow rays, the chloride or bromide will become sensitive to yellow rays; or if mixed with aniline green, which absorbs red rays, the same will be made sensitive to red rays. I denominated these bodies, which sensitize silver salts in the aforesaid manner, *optical sensitizers*, and I and others after me have discovered a large number of such optical sensitizers amongst the dyes, and in this manner the so-called isochromatic gelatine plates, colored with an optical sensitizer such as cyanine, chinoline red, eosine, and erythrosine, are now articles of commerce.

"All these 'isochromatic' gelatine plates are generally less sensitive than ordinary plates, and require a yellow glass plate interposed between the lens and the sensitive plate, for diminishing the power of the blue light. By this interposition of a yellow plate the time of exposure is lengthened, and if the surface of the plate is not quite even, the sharpness of the photograph is lost, so that these 'isochromatic' plates are used on a small scale only for the reproduction of pictures or paintings, but not for portraits or landscape photography."

"Now I have succeeded in making isochromatic gelatine plates, the sensitiveness of which is twice as great as that of the ordinary gelatine plates, and which do not require any yellow plate or screen. This discovery is based:

1. On the application of the eosides of silver—that is, the chemical combinations of eosine dyes with silver. These eosine dyes, or derivatives of fluoresceine, are all acids, and combine with silver to form salts.

2. On the addition of silver salts to other optical sensitizers, for increasing their sensitizing power.

As early as 1884, I observed this favorable influence of the presence of silver salts, and proved, for instance, that eoside of silver will give ten times more sensitiveness for yellow light than ordinary eosine, but I have only now succeeded in making plates without fog, or film, and spots, so that I can introduce the process into practice, and I have proved that it is possible to produce in this manner landscapes and portraits far superior to those taken with ordinary plates.

I have now invented the following methods for making highly sensitive isochromatic plates or sensitizing solutions, so that any photographer or amateur can prepare his own isochromatic plates. In order to attain this object I proceed as follows:

1. Ordinary gelatine plates are bathed in a solution of a soluble salt of silver (1 to 1000), then in a solution of an eosine dye, or a mixture of eosine dyes with other optical sensitizers, with or without liquor of ammonia. The solution of the dye can also be used first, and the silver solution afterwards, or an emulsion can be mixed with a soluble salt of silver and the dye added to the mixture, or *vice versa*, and with or without ammonia.

2. A silver eoside is formed by mixing a solution of an eosine dye, or a mixture of different eosine dyes (for instance, ordinary eosine, blue-tinted eosine, chrysoline, aureosine, phloxine, rose Bengal, or any other derivative of fluoresceine) with a soluble salt of silver, such as sulphate, nitrate, acetate, or fluoride of silver. This eoside of silver can be collected as a precipitate, washed, and mixed with the emulsion, or dissolved in diluted ammonia or diluted acetic acid, and employed as a bath for soaking dry-plates; but I prefer to add liquid ammonia, carbonate of ammonia, or acetic acid, during the process of precipitation, so that the suspended precipitate is dissolved, and to employ the same as sensitizing agent for fluid emulsions, or the said solution can be diluted with water, and used as a bath for dry-plates. The quantity of this solution of eoside of silver to be employed varies according to the quality and kind of emulsion treated with the same, although the following formula will serve as a general guide for those employing my sensitizing solution: 50 cubic centimetres of a solution of an eosine dye (1 part dye to 1000 parts water or diluted alcohol), 1 cubic centimetre of a solution of nitrate of silver (1 part nitrate of silver to 20 parts of water), 1 to 2 cubic centimetres of liquor ammonia. This solution is either mixed with the emulsion—that is, 5 to 10 per cent. is added to the emulsion—or the same is diluted with 200 to 500 cubic centimetres of water, and the gelatine plates immersed or soaked in the same for about one minute, and then dried.

3. I furthermore use other dyes, known as optical sensitizers, which do not chemically combine with silver, but the sensitiveness of which is much improved by the presence of a soluble salt of silver—such, for instance, as cyanine, chinoline red, cœruleine, etc.—and mix them with any soluble salt of silver. I employ, for instance, 50 cubic centimetres chinoline red, or a mixture of chinoline red and cyanine (solution 1 to 1000), with 3 to 5 c.cm. of nitrate of silver (solution 1 to 20), and 15 c.cm. of liquor ammonia. This solution is employed in the same manner as the eoside of silver solution described under (2).

I furthermore employ the solutions described under (2) and (3) in varying proportions for improving the sensitiveness for any part of the chromatic spectrum.

4. I likewise employ, in like manner as mentioned under heads (1), (2), and (3), the salts of lead, which produce, when mixed with an eosine dye, eoside of lead, which said salts can be employed alone, or mixed with eoside of silver.

I furthermore employ the insoluble salts of silver, such as the chlorides, tartrates, citrates, etc., dissolved in ammonia or acid. I do not confine myself to any of the preparations of the mixtures as given in the foregoing specification, as the same can be varied according to requirement, without in any way departing from the nature of my invention.

Having now particularly described and ascertained the nature of my said invention, and in what manner the same is to be performed, I declare that what I claim is:—

(*a*) The employment of the chemical combinations of silver or lead, with an eosine dye or dyes, for producing highly sensitive isochromatic emulsive gelatine plates.

(*b*) The employment of dyes, known as optical sensitizers, in combination with the salts of silver.

(*c*) The employment of various dyes in combination with soluble salts of silver.

(*d*) The manufacture of combinations or solutions of dyes and silver, as strong optical sensitizers for coloring gelatine emulsions, or as a bath for gelatine plates.

(*e*) The application of silver salts not soluble in water, but in ammonia or acid, for the purposes set forth in the foregoing specification.

A "common sense" opinion of the patents of Attout-Tailfer and of Vogel, would be that they were in opposition to each other; but that Dr. Vogel having published to the world in 1873 his cardinal discovery that silver-salts could be "color-sensitized" by means of dyes—neither of them could be valid. But the English law is a curious thing—while English patent law is, well, more curious still. In America careful inquiry into the validity of a patent is made before it is granted, and only a few months ago an inventor known to us who attempted to patent there an article of use in photography (he obtained his English patent without the slightest difficulty) received a reply from Washington directing him to consult the *Photographic News* for 186–, p.—, where he would find a full description of his "invention."

At the date of writing Messrs. B. J. Edwards & Co. possess the sole patent for manufacturing "Isochromatic" plates in the British Isles, while Dr. Vogel's agent (Mr. J. R. Gotz, of 19 Buckingham Street, Strand, London,) sells Dr. Vogel's "Orthochromatic"* plates, manufactured in Germany by Obernetter. The Ilford Company also manufacture isochromatic plates in England, under a license from Mr. Edwards. Dr. Vogel, in 1889, sold a solution of quinoline red and cyanine in alcohol, under the name of "azaline." When ordinary plates were bathed in water to which a few drops of this tincture had been added, they became orthochromatic.

But the modern photographer strongly objects to unnecessary trouble! If he can buy plates already color-sensitized, he will not take the trouble to bathe and dry ordinary plates, and azaline has been but little used in this way.

In America we believe Mr. John Carbutt has been the only maker to prepare commercially an "orthochromatic" dry-plate.

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* The term "orthochromatic" is derived from the Greek, *orthos* correct; and *chroma*, color; and seems somewhat preferable to "isochromatic," although priority should be considered. The Rev. F. C. Lambert, M.A., has proposed the name *Kairo-lamprotic* (from the Greek, *Kairos*, right proportion, and *lamprotes*, brilliancy) for color-sensitive plates; while M. Leon Vidal has still more recently suggested that "orthoscopic," seen correctly, would be a still better name.

CHAPTER XXIV.

THE CHEMISTRY OF SILVER PRINTING: MATT-SURFACE, ALBUMEN, COLLODION, AND GELATINE PRINTS.

Printing With Silver Chloride on a Matt-Surface.

The first successful "photographs" were obtained by exposing opaque or semi-opaque objects to the action of sunlight while upon and in contact with some flat surface coated with a sensitive salt of silver.

As far back as 1727 J. H. Schulze printed letters and signs by means of sunlight upon a mixture of nitrate of silver and chalk. The great Swedish chemist, Scheele, made a classical investigation into the action of light upon silver chloride in 1777; and between 1790 and 1802 Thomas Wedgwood and Humphry Davy obtained prints of "paintings on glass," leaves, wings of insects, and the shadows or profiles of opaque objects by means of paper or leather coated sometimes with nitrate of silver, sometimes with chloride of silver. But as even such a skilful chemist as Davy was unable to devise any means of "fixing" these prints, the process was abandoned as useless.

Talbot's "Photogenic Drawing."—Between 1835 and 1839 Henry Fox Talbot, an English gentleman of high rank, succeeded in devising a printing process which produced a surface highly sensitive to light. Paper was coated with a weak solution of common salt, and a solution of nitrate of silver was then brushed over it, the strength of the solutions being so adjusted as to leave a *slight excess* of the silver nitrate. Such paper was a hundred times more sensitive to light than paper coated with either the chloride alone or the nitrate alone.

Let us see what were the chemical changes involved

$$\underset{\substack{\text{Silver}\\\text{Nitrate}}}{AgNO_3} \quad \underset{\textit{and}}{+} \quad \underset{\substack{\text{Sodium}\\\text{Chloride}}}{NaCl} \quad \underset{\textit{produce}}{=} \quad \underset{\substack{\text{Silver}\\\text{Chloride}}}{AgCl} \quad \underset{\textit{and}}{+} \quad \underset{\substack{\text{Sodium}\\\text{Nitrate.}}}{NaNO_3}$$

The common salt (sodium chloride) combines with the silver nitrate, and silver chloride is produced. Sodium nitrate is also produced; but this may be neglected, as it takes no further part in the work.

It seems strange that the paper coated with silver chloride, *containing in addition a little silver nitrate*, should be so much more sensitive to light than paper coated with the pure silver chloride alone. This is explained by the fact now known to us that perhaps no substance is sensitive to light when perfectly pure, dry, and isolated. The action of light is undoubtedly—as Scheele proved in 1777—to separate a part (or the whole) of the non-metal (the chlorine in this case) from the metallic silver with which it is combined.

$$2AgCl = Ag_2Cl + Cl$$

Silver Chloride *produces* Silver Sub-chloride *and* Chlorine.

Let us suppose the above equation to represent the action of light upon ordinary white silver chloride. We see that a part of the chlorine is driven off, while dark-colored silver sub-chloride remains. But unless there be some substance present with which the liberated chlorine can combine (as water, or, better, silver nitrate) the light is unable to decompose the silver chloride. This can be proved by exposing dried AgCl to sunlight in a glass tube from which air has been extracted; its color is unchanged.

Albumen Introduced in Silver Printing (*in* 1850) *to Impart a Glossy Surface to the Paper.*—This printing method, upon paper coated with silver chloride, and with slight excess of silver nitrate, which was published by Fox Talbot on January 31, 1839, has remained the chief printing process in use in photography right down to the present day.

From 1839 to 1850 the paper was always left with its natural or "matt" surface. But in the latter year Blanquard Evrard and Gustave Le Gray, in France, introduced the plan of giving the paper a preliminary coating of albumen (white of egg) by which the surface of the paper was made very glossy, the details brought out and the image prevented from sinking in. This albumenized paper was introduced into England by Talbot and Pollock in 1852–3.

During the last two or three years, however, a strong reaction has set in against this inartistic gloss, though for ordinary portrait work it still maintains its sway.

Modern Printing in Silver.—The photographic journals of the present day usually contain advertisements of "albuminized paper," and also of "ready sensitized" paper. The first of these has to be sensitized by the purchaser—usually the professional photographer; while the latter is preferred by the amateur, as it is ready to be at once placed in the printing-frame.

Preparation of Albumenized Paper.—Albumenized paper is albumenized and "salted" at the same time. The following mixture is prepared:

Fresh white of eggs	7 ounces
Ammonium chloride	75 grains
Alcohol	2 drams
Distilled water	2 ounces

Dissolve the NH_4Cl (ammonium chloride) in the alcohol and water; add it to the albumen, and beat up vigorously. Filter through cotton-wool which has been steeped in water. This quantity should be amply sufficient for a quire of paper. Place the mixture in a dish, and float each sheet of paper upon it, in turn, for one and a quarter minutes, taking care to avoid bubbles. Then hang the paper up by two corners to dry.

Double albumenized paper is made by exposing the paper, coated as above, to a current of steam by which the albumen is coagulated and hardened. The paper is then floated on a *second* bath of albumen. Such paper has an extremely glossy surface, but it is more liable to crack and blister.

Some commercial makes of albumenized paper have a very unpleasant smell. This is usually due to *fermented* albumen having been used in their preparation, a method which is in favor with some large firms on the Continent. Such paper will generally give fine tones. Sometimes, however, the albumen used has been allowed to become partially decomposed, or putrid, and the smell of sulphuretted hydrogen then produced is not only offensive but may be dangerous to the permanence of the prints.

Albumenized paper is made so well (commercially) and sold so cheaply that we are not aware that any practical photographer has ever found it "pay" to albumenize his own.

SENSITIZING ALBUMENIZED PAPER.

A "bath" of silver nitrate must be made up by dissolving the pure crystallized salt in distilled water. The strength of this solution may vary from 30 grains (not less) per ounce for hard negatives with strong contrasts, to 80 grains per ounce for thin weak negatives. The best average strength is 60 grains per ounce.

The quantity of this solution to be made up for use varies with different workers, and with the size of the pieces to be sensitized. When sheets of albumenized paper of the full size (17½ by 22½ inches) are to be floated on the solution, about a gallon of it will be necessary. In any case it should be not less than half an inch deep in the flat shallow dish usually employed. The paper should be kept in a damp place for an hour or two before sensitizing; and it may be floated on the silver bath for two minutes (in summer) or three minutes (in winter). The chemical change that takes place during the floating may be thus expressed:

$$\begin{array}{ccccccc} AgNO_3 & + & NH_4Cl & = & AgCl & + & NH_4NO_3 \\ \text{Silver} & \textit{and} & \text{Ammonium} & \textit{produce} & \text{Silver} & \textit{and} & \text{Ammonium} \\ \text{Nitrate} & & \text{Chloride} & & \text{Chloride} & & \text{Nitrate.} \end{array}$$

Silver albuminate is also formed; but its chemical composition is very complex and uncertain, and its presence is neither desirable nor necessary.

The paper is drawn over the edge of the dish to remove the otherwise too great excess of the bath solution which would cling to it; and is then either hung up at once by the corners to dry, or is first pressed between sheets of chemically pure white blotting-paper.

The worst thing about freshly sensitized paper like this is that it discolors if kept for more than two or three days. By keeping it between sheets of blotting-paper which have been soaked in carbonate of soda solution (1 to 20), and then dried, it may be kept white for two or three weeks. But its advantages are that it enables black tones to be got more easily, and that the paper can be sensitized (by the use of a weak or of a strong bath) to suit negatives of varying qualities.

The silver bath must not be acid. If it turns blue-litmus paper red (proving acidity), add a few drops of sodium carbonate solution until the blue color is just restored.

"Ready-Sensitized" Paper.—If albumenized sensitized paper will not "keep," the student may inquire how it is that paper of this description can be purchased from store-dealers which is warranted to keep for several months—sometimes for a year? The answer is, that such "ready-sensitized paper" has undergone a special treatment. What the exact nature of that treatment may be is rigidly preserved as a "trade secret," and the practice of different firms probably varies.

The following methods for the production of "ready-sensitized paper" have been published:

1. Add ten drops of perchloric acid to every ounce of the sensitizing bath of silver nitrate.

2. Or, after removal from the bath, and when the paper has become surface-dry, float the *back* of the paper for one minute upon a solution of citric acid thirty grains to every ounce of water. The citric acid combines with the silver nitrate to form silver citrate, which a much more stable salt than the nitrate.

3. Or, similarly, float the previously sensitized paper on the following solution:

Picked white gum arabic, dissolved in six pints of water	6 ounces
Citric acid	2 ounces
Tartaric acid	2 ounces
Hydrochloric acid	2 ounces

Float the *back* of the sensitized paper on this mixture for from half a minute to five minutes, according to the length of time the paper is required to keep.*

4. If the sensitized paper be *washed*, by floating it after sensitizing and when surface-dry, upon two or three changes of distilled water, it will keep for two or three weeks. The reason is, that the water removes nearly all the free silver

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*Ashman's "Lessons in Silver Printing."

nitrate. But such paper will not tone unless it be *fumed* before printing.

5. Sensitized paper keeps well if all moist air be excluded. This can be done by placing the paper in air-tight tins (like those used by the Platinotype Co.) containing calcium chloride.

Ready-sensitized paper is very convenient, and is largely used not only by amateurs but by professionals. It does not tone so readily, nor are black tones so easily obtained as with freshly sensitized paper. Before printing, it should be "fumed"; or, after printing and before toning, the prints should be soaked in a weak alkaline solution (see *toning*) to neutralize the acid by which the paper has been preserved.

"*Fuming Sensitized Paper.*"—It is a common practice in America—much less so in England—to expose each sheet of sensitized paper before printing for about ten minutes to the fumes of strong ammonia, placed in a saucer in an air-tight box, to the lid of which the paper is pinned. The volatile alkali (as ammonia is termed) destroys any free acid which may be present in the paper.

Printing on Matt-Surface Paper.—The reaction against a glossy surface has lately led to a return by many workers to the practice which was universal before 1852—the printing in silver upon "matt" or "dead" surface paper.

The paper must be *pure.* Especially it must be free from chlorine and also from hyposulphite of soda, which is largely used by paper-makers as an "anti-chlor" or substance to remove the chlorine. Almost any good white paper will answer the purpose. Recent researches have shown that it is hardly possible to purchase a sample of paper which does not reveal the presence of "hypo" when delicate tests are employed. This is much to be regretted.

The effect of printing upon paper with quite a rough surface has, during the last year or two, been much admired. For such an object Whatman's drawing-papers have been used, and Mr. Lyonel Clark* recommends the paper sold as "Arnold's pure unbleached."

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*Salting and Exciting of Drawing and other Commercial Papers: *Camera Club Journal*, January and November, 1890.

The paper may, or may not, require *sizing*. Blotting paper is unsized, while some varieties of glossy writing paper are nearly all sized. The *rough* paper will certainly need sizing, and may be passed through a warm solution of gelatine of the strength of from 12 to 24 grains per ounce of water. It must then be hung up to dry.

The next thing to do is to *salt* the paper. For this purpose float the dry paper for three minutes on—

Ammonium chloride	130 grains
Sodium carbonate	3 grains
Water	1 pint

Hang up to dry in a warm room.

Sensitizing with Ammonio-Nitrate of Silver.—To sensitize this paper we may use the ammonio-nitrate bath, first recommended by Dr. Taylor in 1841, and improved by T. F. Hardwich in 1855. It is especially useful for weak negatives and for printing in dull weather.

Dissolve 60 grains of silver nitrate in half an ounce of distilled water. To this add ammonia, drop by drop, until the black precipitate first formed is just redissolved. The liquid should be stirred continually with a glass rod.

Divide the solution into two parts, and to one part add nitric acid, drop by drop, until the color of blue litmus is just changed to red. Then mix the two parts together, and add enough water to make up to 1 ounce. Filter, if not perfectly clear.

How to Apply the Ammonio-Nitrate Solution.—It is best to apply this sensitizing solution with a *brush*. A camel-hair brush may be used, but it soon becomes spoiled and useless. The best method is to use a "Blanchard's Brush," named after its inventor, the well-known English professional, Valentine Blanchard. It is made by folding a double thickness of swan's-down calico over the end of a strip of glass from three to six inches wide. The calico must be tied on, or secured to the glass by a rubber band. A pool of the sensitizing solution is poured upon one end of the sheet of paper (laid on a flat surface, as a sheet of glass), and this is led over the paper with the brush. The paper should be thoroughly moistened in every part with the solution. It may lie for a minute to allow the solution to soak in, and should then be hung up near a fire to dry.

This paper will keep for a week or two if preserved between sheets of soda blotting paper.

Action of Light upon Sensitized Paper.—When "sensitized paper" is spoken of in photography, the ordinary albumenized paper containing chloride of silver (plus a little nitrate) is always meant.

When such paper is exposed to light its white surface is gradually changed in hue, passing through various shades of brown, gray, and violet, to a brown or violet black.

What is the precise chemical change produced by the action of light upon the silver chloride? That has long been—and still remains—one of the puzzles of photographic chemistry. The subject is treated of in greater detail in discussing the "latent image"; but it will suffice here to say that in the present state of our knowledge the following equation represents more nearly than any other the probable facts:

$2\,\mathrm{AgCl}$ $=$ $\mathrm{Ag_2Cl}$
Silver chloride, *when decomposed by light, produces* silver sub-chloride
$+$ Cl
and chlorine.

Chlorine is undoubtedly given off—Scheele proved that in 1777—but whether it is entirely or only in part separated from the silver is still doubtful.

Printing-Papers with Glossy Surfaces Obtained Otherwise than by Albumen.

After the introduction of albumen to give a surface gloss to prints about the year 1850, the desire for a highly-polished surface (mainly, and especially for portrait work) so increased that many endeavors were made to satisfy it.

The employment of *double*-albumenized paper we have already mentioned. There is no doubt but that the second coating with albumen enables a superior degree of glossiness to be obtained, and that this gloss does throw up and relieve the shadows, and brings out the details.

Blanquart-Evrard Varnishes Prints with Gelatine (1857).—The great French professional printer, M. Blanquart-Evrard, of Lille, proposed, in 1857, to protect and strengthen prints by a varnish composed of gelatine and tannic acid. A reference to this method in the *Photographic News* for 27th May, 1858, called forth a letter from an English worker, Mr. W. L. Scott (June 17), in which he stated that he had practised such a process for two or three years. The prints were dipped in a warm solution of pure gelatine, dried, and then soaked in a colorless solution of tannic acid (200 grains to the pint) for ten minutes. After drying, they were immersed in the same solutions over again, and finally rinsed and dried. This process gave a high gloss to the paper, and was believed to render the prints more permanent. The action of the tannin is, of course, to harden the gelatine—to convert it into a sort of transparent leather, in fact.

Burnishing and Rolling Prints.—The use of a "flat-iron" to level the surface of a mounted print may not impossibly have occurred to some worker of Talbot's "photogenic" process, even as early as 1839. Nay, it is possible that the advantage of using the said flat-iron hot instead of cold may have been discovered at quite as early a date; but this genius, strange to say, did not patent his "application" of the useful domestic implement to this purpose of high art, and consequently his name has not come down to us.

Up to the year 1858 portraits were all but invariably made by professional photographers, either upon silver plates (daguerreotypes) or with collodion upon glass. In either way, the finished portrait was placed in a suitable case—*a passe-partout*, or a frame—before being delivered to the customer; indeed its delicate nature made this inevitable.

But in 1858 the mania for the *carte-de-visite* sprang up. Everybody desired to present his or her card-portrait to everybody else; and the professionals reaped a golden harvest for several years. But with the advent of the positive paper-print stuck upon cardboard, the flat-iron came out in great force again. Then it quickly dawned on some inventive genius that, by passing the mounted prints between steel *rollers*, the flattening and smoothing would be rapidly and effectually accomplished. Lastly, it was found that if a hot steel bar or plate were substituted for the lower roller, the prints were *burnished* to a degree that gave them a surface almost equaling glass; and such instruments—called "burnishers"—have proved all but indispensable to the professional portraitist ever since.

Printing in "Wothlytype."

The name of Wothly (or Wothlij) is unknown to the present generation of photographers; but twenty-seven years ago his printing process created quite a sensation, and the "United Association of Photography," with Colonel Stuart Wortley at its head, was formed to purchase the patent and to work it commercially in England. The English patent itself is dated 24th September, 1864. Paper was sized with arrowroot and then rolled. It was then coated, of course in a dark-room, with collodion in which silver nitrate and uranium nitrate had been dissolved. The paper having been dried, was printed out beneath a negative in the usual way. It was then toned and fixed as usual.

All sorts of foolish claims were made for Wothlytype. It was puffed in the *Times* in the autumn of 1864, and was said to be very cheap and capable of giving permanent results. As a matter of fact, the patent contained little that was new. In 1857, the Scotchman, Burnett, had described all the facts about uranium printing. The truth is that M. Wothly was an excellent operator and a good man of business. He produced first-class negatives and made exquisite prints from them. He sold his patent; but he could not sell the skill to which—and not to the patent—the production of his capital "specimens" was due. Wothlytype ran but a brief race; after a year or two nothing more was heard of it. But it doubtless furnished Simpson with the idea of the collodio-chloride printing process, which we shall next describe.

Printing with Collodio-Chloride of Silver: Simpsontype.

At the close of the year 1864, Mr. G. Wharton Simpson (then editor of the *Photographic News*) announced in the

"Year Book" or almanac connected with the same periodical, that he had "discovered that chloride of silver may be held in suspension in collodion in a state of subdivision so exceedingly fine that it may be used in this form for coating paper, and gives then, with the usual manipulation, exceedingly fine prints, in which, when finished, *no silver is found in the whites*." The process was developed and perfected during 1865 and 1866; but although beautiful results were obtained —especially upon opal glass—the collodio-chloride printing process never came into general use.

In practice the paper was first sized with arrowroot to prevent the emulsion from sinking in. Chloride of silver was then formed *in* collodion, by shaking up in it nitrate of silver with chloride of strontium.

$2AgNO_3$	+	$SrCl_2$	=	$2AgCl$	+	$Sr(NO_3)_2$
Silver		Strontium		Silver		Strontium
Nitrate	*and*	Chloride	*produce*	Chloride	*and*	Nitrate

The paper was coated by laying it upon a flat surface, turning up its edges all round, but leaving a corner from which to pour; the emulsion was then poured on and off just as in coating a glass plate. The paper so prepared was dried, and then printed-out, toned, and fixed in the usual way.

Collodio-chloride paper was manufactured, commercially, on the Continent, by Herr Obernetter.

It is unrivalled for the delicacy of the detail which it brings out; and is specially suited for printing from thin and weak negatives.

It was also made and sold by another Continental firm under the name of "leptographic paper."

Aristotype and Obernetter Papers.—During the last two or three years collodio-chloride has again been resuscitated; and has been sold as "aristotype" and "Obernetter" paper. But other papers coated with *gelatino*-chloride of silver have also been sold under these names, and it is a matter of some importance to be able to distinguish between them. This may be effected by treating a *print* with wood-naphtha, which will dissolve collodion, but which has no effect upon gelatine.

CHAPTER XXV.

THE CARBON PRINTING PROCESS AND ITS CHEMISTRY.

Permanence of Carbon.—The element whose proper name is carbon, but which assumes such different forms as the diamond, coke, lamp-black, charcoal, etc. (each and all of which are composed of nothing but carbon), is perhaps the most *permanent*, under ordinary conditions, of all the substances with which chemistry has made us acquainted. In the form of "printer's ink," carbon assures the permanence of books, engravings, etc.; and in the ancient papyri of Egypt we have manuscripts written in carbon which are as easy to decipher now as they were thirty centuries ago. No wonder that photographers in their search for a permanent printing process turned their eyes longingly to carbon early in the history of the photographic art.

Ponton Discovers the Action of Light on Bichromate of Potash.—In 1839, Mungo Ponton, a Scotch experimenter, announced * the fact that paper coated with a solution of potassium bichromate was turned brown by exposure to light. Any one can repeat this experiment by floating writing paper upon a 10 per cent. solution of the bichromate, and then exposing the dried paper to sunlight beneath a negative or an engraving. Such a print is "fixed" by simple washing in water, which removes the unaltered and still soluble bichromate.

Becquerel Shows that a Colloid must be Present.—In repeating Ponton's experiment the great French chemist, E. Becquerel, found that the *size* in the paper played an important part in the reaction.

Talbot Discovers that a Mixture of Gelatine and Potash Bichromate is Rendered Insoluble by Exposure to Light.—

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* *Edinburgh New Philosophical Journal*, Vol. XXVII,, pp. 169–171.

Unless some colloid body (as glue, gelatine, starch, etc.) be present, the bichromate of potash is not affected by light. But Talbot found that when the bichromate was mixed with some colloid (the "size" in paper is only weak glue) the effect of exposure to light was not merely a change of color, but the colloid body *was rendered insoluble* in liquids in which it had previously been soluble. This important fact was discovered by Henry Fox Talbot in 1852, and was patented by him as part of a photo-mechanical printing process which he called "photoglyphic engraving," on October 29th in that year.

Poitevin, Sutton, and Pouncy obtain Carbon Prints.—The French chemist, A. Poitevin, in 1855 added powdered carbon to Talbot's mixture of bichromate and glue (or other colloid). Paper was coated with this mixture, dried, exposed to light beneath a negative, and then washed in warm water. The glue, etc., unaffected by light was dissolved away, leaving the insoluble glue (holding carbon, and therefore colored) to form a positive picture. In England, Thomas Sutton and John Pouncy discovered the same process, independently, in 1858; and long accounts of it were printed in the periodical edited by Sutton, *Photographic Notes*, in 1858–59; and also in a little book, "Photography in Printing Ink," which Sutton wrote in 1863. The black color of printing ink is, of course, due to finely-divided carbon.

Half-Tones wanting in the Early Carbon Prints.—The light, acting through the negative, affected the *surface* of the carbon print beneath. In the deepest shadows of the picture (represented by clear glass in the negative) the light had time to render the carbon tissue * beneath, insoluble right down to the paper backing. Under the "high-lights" (represented by a dense and opaque deposit of silver in the negative) the tissue is quite unaffected and remains soluble. But under the "half-tones" of the negative the tissue is affected to depths varying with the opacity of the deposit of silver representing the half-tones. When the tissue is removed, and its surface washed, the layer of soluble gelatine which remains *beneath* the insoluble surface parts, representing the half-tones, is dissolved away, and it usually *carries away the upper layer with it.* Thus only a hard, black-and-white carbon picture remains. This fact was clearly pointed out by the Abbé Laborde in a communication relating to an analogous process made to the French Photographic Society, in 1858.

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* The thin paper coated with a mixture of gelatine, bichromate of potash, and powdered carbon, is called "carbon tissue."

Half-Tones secured by Burnett (1858) and by Fargier (1860).—The Scottish experimenter, J. C. Burnett, proposed * in 1858 the remedy of placing the *back*, or uncoated side of the paper next the negative; but this was impracticable, because of the very long exposure thereby rendered necessary; and because the texture of the paper was imparted to the print.

The real remedy for the lack of half-tones in carbon printing was patented by a Frenchman named Fargier, in September, 1860. It consisted in stripping off the paper back of the tissue, and then applying the solvent, the warm water, *to the back* of the carbon film. To do this, it was necessary to strengthen the film by a coating of collodion applied to its face. Good prints in carbon now became possible; but the manipulations under Fargier's method were very difficult.

Swan, Johnson and Sawyer make Carbon Printing a Practical Success.—The patent of the English worker, J. W. Swan, dated 28th February, 1864, for the first time put a really practical, successful, and comparatively easy means of producing carbon prints before the photographic world. And yet Swan's improvements may be considered as only "details"; but it is just these details which make all the difference between failure and success. He mixed a little sugar with the gelatine to render it less brittle when dry. After exposure beneath a negative, the print was stuck, face down, on either a temporary or a permanent support; and the paper backing, with the soluble gelatine beneath it, was washed away with warm water. The picture was thereby "developed"—or rather *made visible.* But by the single transfer it was, of course, *reversed.* In some cases this reversal does not matter; but, usually, it is necessary to again transfer ("double transfer") the carbon print to a second and permanent support or backing. Or, if a reversed negative be made to begin with, by placing a prism, or a mirror, in front of the lens, then the single transfer only is necessary. Swan also introduced many other powdered colors, as red chalk, etc., in place of carbon; so that pictures in any tint could be obtained. But of course these lacked the permanence which is the great recommendation of carbon. Swan used many adhesives to make the carbon tissue adhere to its various "supports"; but in 1869 J. R. Johnson showed that it was only necessary to first soak the carbon tissue in water for a short time, in order to enable it to adhere to any water-proof support. Lastly, in 1874, J. R. Sawyer patented a "flexible support," consisting of water-proof waxed paper, which most conveniently supported the tissue while it was being developed.

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* *Photographic Journal* for 22d November, 1858.

In the following year—1875—two French photographers who possessed excellent powers of manipulation, exhibited the carbon process in practice in most large towns in England and on the Continent; and succeeded at last in drawing general attention to its many excellent points. It was then thought that carbon printing would displace silver; but the idea has proved fallacious. The glossy silver print has held its own; though there are not now wanting signs which seem to show that its reign may not be of much longer duration. The Autotype Company, of London, established by Swan and his partners, has done much for the advancement of carbon printing; while on the Continent a similar good work has been performed by the firm of A. Braun, of Dornach.

Practical Carbon Printing.—Just as in silver-printing, the carbon tissue can be bought either sensitized or unsensitized. In appearance it resembles black American oil-cloth. The plain or unsensitized tissue consists of paper coated with a solution of gelatine and sugar, to which refined lamp-black has been added.

The bichromate of potash—which is the sensitizing ingredient—can either be added to the above substances before coating, or the coated paper may be sensitized by floating it upon a 4 per cent. solution of the bichromate, to which a little ammonia has been added. After sensitizing, the carbon tissue will not keep good for more than ten or fourteen days.

The black tissue is exposed to sunlight beneath a negative in the usual way. The negative must have a "safe-edge" about the eighth of an inch wide, painted all round it in any opaque black varnish. This is to insure the adhesion of the margins of the tissue to the support during development. The ordinary ready-sensitized carbon tissue is a little more rapid than ordinary albumenized paper. If, therefore, it be printed along with the latter, each under a negative of average density, when the one is done the other will be done. A special instrument, called an actinometer, is generally used to determine the time of printing.

Four dishes are necessary for development. The first contains cold water and a piece of waxed "flexible temporary support." The exposed carbon tissue is soaked in cold water for a couple of minutes, and is then squeegeed down upon the support. It is placed between blotting-paper, and left under gentle pressure for twenty minutes. After this space of time the carbon tissue is placed in a second dish containing water, at 100 deg. F. In a minute or two the paper backing may be stripped off, and by dashing the warm water upon the print the still soluble part of the gelatine may be washed away, and the picture revealed. The print is then washed in cold water in a third dish. The fourth (and last) dish contains a saturated solution of common alum. The now developed print is soaked in this till all the yellow tint (due to the bichromate) has disappeared. It is then washed in several changes of plain water to get rid of the alum. The final operation consists in squeegeeing a piece of "permanent support" (paper coated with soluble gelatine) upon the print, which is then allowed to dry. As the carbon print dries it separates itself from the waxed surface of the "temporary support"; but adheres firmly to the "permanent support." It may then be trimmed and mounted in the ordinary way.

All the "supports" and other materials named are prepared commercially, of great excellence and moderate in price.

It is far better to purchase them than to attempt to make them, except for the sake of experiment.

Chemistry of the Carbon Printing Process.—In the paper by Mungo Ponton, already alluded to, and which he published in 1839, he describes clearly and forcibly the effect of light upon potassium bichromate. Ponton writes:—"Paper immersed in bichromate of potash is powerfully and rapidly acted upon by the sun's rays. * * * When an object is laid in the usual way on this paper, the portion exposed to the light speedily becomes tawny, passing more or less into a deep orange, according to the strength of the solution and the intensity of the light. The portion covered by the object retains the original bright yellow tint which it had before exposure, and the object is thus represented yellow upon an orange ground, there being several gradations of shade or tint, according to the greater or less degree of transparency in the different parts of the object.

"In this state, of course, the drawing, though very beautiful, is evanescent. To fix it, all that is required is careful immersion in water, when it will be found that those portions of the salt which have not been acted on by the light are readily dissolved out, while those which have been exposed to the light are completely fixed on the paper. By this second process the object is obtained white upon an orange ground, and quite permanent."

Ponton's bichromate pictures may have appeared "beautiful" to his astonished eyes, but it is to be feared that they would not gain many admirers now-a-days.

In the presence of some organic material, as the fibre of paper, the size with which the paper is usually coated, etc., bichromate of potash undergoes the following decomposition when exposed to light:

$$K_2Cr_2O_7 = K_2CrO_4 + CrO_3$$

Bichromate of potash *produces* Chromate of Potash *and* Chromic Acid.

The chromic acid is then further decomposed as follows:

$$CrO_3 = CrO_2 + O$$

Chromic Acid *produces* Chromium Peroxide *and* Oxygen.

The chromium peroxide is of a tawny color, and—by its contrast with the bright yellow bichromate—produces the picture. But by prolonged exposure to light, the chromium peroxide loses another atom of oxygen, and becomes reduced to chromium sesquioxide, thus:

$$\underset{\substack{\text{Chromium}\\\text{Peroxide}}}{\mathrm{2CrO_2}} \quad \underset{\textit{produces}}{=} \quad \underset{\substack{\text{Chromium}\\\text{Sesquioxide}}}{\mathrm{Cr_2O_3}} \quad \underset{\textit{and}}{+} \quad \underset{\text{Oxygen.}}{\mathrm{O}}$$

This chromium sesquioxide is of a greenish tint, and the contrast which it produces with the bichromate is not so marked; hence by long exposure the picture becomes weaker.

Now what becomes of the oxygen which is liberated? It combines with any colloid substance (as gelatine) which may be present, and renders it insoluble. This was very clearly explained by Poitevin in a book* which he published in 1862: "The chromic acid loses (by exposure to light) a part of its oxygen, which combines with the organic matter and renders it insoluble. When the film is washed, the carbon remains adhering to the exposed insoluble parts, and forms the picture." As to the precise nature of the oxidized gelatine product formed, most of what we know is due to the researches of Dr. Eder, published † in 1878; but the subject is a difficult and obscure one. Captain Abney gives the following equation (which we have simplified) as representing the final action of the bichromates upon organic matter generally:

$$\underset{\substack{\text{Organic}\\\text{Matter}}}{\mathrm{Cx\,Hy\,Oz}} \quad \underset{\textit{and}}{+} \quad \underset{\substack{\text{Potassium}\\\text{Bichromate}}}{\mathrm{K_2Cr_2O_7}} \quad \underset{\textit{produce}}{=} \quad \underset{\substack{\text{Potassium}\\\text{Hydrate}}}{\mathrm{2KHO}} \quad \underset{\textit{and}}{+}$$

$$\underset{\substack{\text{Chromium}\\\text{Sesquioxide}}}{\mathrm{Cr_2O_3}} \quad \underset{\textit{and}}{+} \quad \underset{\substack{\text{Oxidized}\\\text{Organic Matter.}}}{\mathrm{Cx\,Hy\,Oz\,OO}}$$

In this equation the letters x, y, and z are used simply to denote indefinite quantities of each element. The oxidized organic matter (gelatine, etc.) is found to be insoluble in liquids in which the ordinary organic matter is quite soluble.

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[*] "L'impression photographique sans sels d'argent." Paris: Leiber, 1862.

[†] "Ueber die Reactioner der Chromsäure und der Chromate auf Gelatin, Gummi, Zucker, etc." Wien, 1878.

Dr. Paul E. Liesegang has written an excellent "Manual of the Carbon Process,"* which should be studied by all who desire to practice this excellent and permanent method of photographic printing.

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* Translated from the German, and sold by The Scovill & Adams Co.

CHAPTER XXVI.

PRINTING WITH SALTS OF IRON—CYANOTYPE AND KALLITYPE.

Herschel Publishes the Cyanotype Process in 1842.—In a valuable paper entitled "On the Action of the Rays of the Solar Spectrum on Vegetable Colors, and on some new Photographic Processes," written by Sir John F. W. Herschel, and published in the *Philosophical Transactions* for the year 1842, we find the common "blue process" of the present day described under the name of *cyanotype*. The process appears to have "sprung full-fledged" from Herschel's brain; for the exact method he gives will produce excellent results, and has been little varied since. It is often called the "ferro-prussiate process," from the names of the two chemicals which are employed in it.

Cyanotype in Practice.—The "blue process," or cyanotype, deserves to be more widely known and practiced than at present. It is more favored in America than in England. It is very cheap, very clean, easy to work, and the results are permanent. The blue color suits many subjects admirably. The paper to be used should be well sized, in order to keep the chemicals as far as possible on the surface; otherwise the picture has a dark and sunken-in appearance. Highly-sized white note-paper answers well. Or any paper can be sized by making arrowroot into starch and sponging it over the paper to be used, which must then be dried. If ordinary albumenized (not sensitized) paper be soaked for a minute in boiling water, to coagulate the albumen, it will yield very brilliant blue prints.

Make up the following solutions:

No. 1.

Ammonio-citrate of iron	1 ounce
Distilled water	4 ounces

No. 2.

Red prussiate of potash	1 ounce
Distilled water	4 ounces

These solutions must be kept in separate bottles, which should have brown paper glued round them, to protect the contents from the light.

Ammonio-citrate of iron is sold at most druggists' shops as "citrate of iron and ammonia." Its chemical formula is:—

$$(C_6H_5O_7)_3Fe_2\,(NH_4)_3$$

The red prussiate of potash is more properly named "ferridcyanide of potassium"—$K_3\ FeCy_6$.

Mix the solutions 1 and 2 in equal proportions in a clean glass dish, and add for each ounce of the mixture 5 drops of a 10 per cent. solution of ammonium bromide. Mix well by stirring with a glass rod. The liquid so prepared is sensitive to light, and the operation of coating the paper to be used should be done by gas-light or in a dark corner of a room. The paper to be sensitized may be floated upon or soaked in the solution for two or three minutes; when lifted out it should be drawn over a glass rod to remove the excess of the liquid. The paper may also be laid upon a sheet of glass or a board, and the mixture applied to its surface by means of a clean sponge. In any case the paper should be dried in a dark room near the fire. The sooner it is used the better; for although cyanotype paper will keep fairly well for days, or even weeks, it never gives such bright blue tints as when just freshly prepared.

Cyanotype paper is printed beneath a negative in the usual way; it takes two or three times as long to print as ordinary silvered paper. When done, the picture can be plainly seen in brown and yellow, the shadows being bronzed. Now remove the print from the printing frame and immerse it in water, to which a little hydrochloric (or citric) acid has been added (just enough to make it taste sour). Finally wash in five or six changes of plain water. The result should be a brilliant print in blue lines upon a white ground.

Chemistry of the Cyanotype Process.

It is easy to reduce the ferric compounds (or "per-salts of iron," as they used to be called) to the ferrous state (= "protosalts") by chemical means alone. Thus, nascent hydrogen is capable of effecting this change, converting ferric sulphate into ferrous sulphate.

$Fe_2(SO_4)_3$ + H_2 = $2FeSO_4$ +
Ferric Sulphate *and* Hydrogen *produce* Ferrous Sulphate *and*
H_2SO_4
Sulphuric Acid.

Light is also capable of effecting such a change in ferric compounds; but there must be some substance present, some "sensitizer," which is capable of combining with the oxygen or other non-metallic substance given off by the ferric salt. Take ferric chloride, Fe_2Cl_6; light has no effect upon this substance when simply dissolved in water, because the water is incapable of combining with the chlorine. But when ferric chloride is dissolved in alcohol and exposed to light, the following change takes place:

Fe_2Cl_6 + C_2H_6O = $2FeCl_2$ +
Ferric Chloride *and* Alcohol *produce* Ferrous Chloride *and*
C_2H_4O + $2HCl$
Aldehyde *and* Hydrochloric Acid.

In the ordinary "ferro-prussiate paper," the paper itself and the "size" with which it is coated are able to act as sensitizers. The paper is coated with ammonio-citrate of iron (though ferric chloride and other ferric salts will answer). On exposure to light the iron salt is reduced to a ferrous state—some of its oxygen, etc., being removed—though the precise composition of the substances formed is hardly known with certainty; but that is immaterial. The main point to remember is that light *changes* (when a suitable "sensitizer" or halogen absorber is present) *ferric salts into ferrous salts.*

The advantage of the change, photographically speaking, is this: *Ferric* salts are unaltered when mixed with red prussiate of potash; *ferrous* salts form a blue precipitate with the same substance.

$6FeCl_2$ + $4K_3FeCy_6$ =
Ferrous Chloride *and* Potassium Ferridcyanide *produce*
$2Fe_3(FeCy_6)_2$ + $12KCl$
Ferrous Ferridcyanide *and* Potassium Chloride.

The ferrous ferridcyanide is a fine blue solid, long known in commerce as "Turnbull's Blue," and used as a paint.

Thus light, acting through a negative upon the ferro-prussiate paper beneath, converts the ammonio-citrate of iron into a ferrous salt, more or less completely according to the relative transparency of the different parts of the negative. Under the opaque parts no change takes place. By floating upon water, the substances with which the paper is coated are all brought into solution, and they then act chemically upon one another, with the result that a picture in blue lines upon a white ground is produced in the way described above.

It is quite possible to coat the paper with the ammonio-citrate of iron only; and then, after exposure to light, to develop it by floating upon a solution of the red prussiate of potash.

The Kallitype Printing Process—Kallitype No. I.

The "kallitype" process takes its name from the same two Greek words, signifying "beautiful picture," from which Fox Talbot derived the name of his "calotype" negative process, patented by him in 1841. As the two words sound very similarly they are liable to be confounded, and it seems a pity that some more distinctive name was not chosen.

"Kallitype" was patented in 1890 by the inventor, Dr. W. W. J. Nicol, lecturer on chemistry at the Mason College, Birmingham, the number of the specification being 5,374. (February 15, 1890.)

The principle of kallitype consists in exposing to sunlight, beneath a negative, paper coated with ferric oxalate. The action of light is to reduce this substance to ferrous oxalate:

$Fe_2(C_2O_4)_3$	$=$	$2Fe\,(C_2O_4)$	$+$	$2CO_2$
Ferric Oxalate	*produces*	Ferrous Oxalate	*and*	Carbonic Acid Gas.

The exposed paper is then developed by floating it for fifteen seconds upon the following solution, used cold:

Nitrate of silver	50 grains
Citrate of soda	1 ounce
Bichromate of potash	1 grain
Water	10 ounces
Strong ammonia	½ drachm

To prepare this developer, dissolve the silver nitrate in about 1 ounce of the water, and the soda and potash in the remainder, and mix. Then add the ammonia and filter.

The chemical action of this developer can hardly be represented by equations; but it is plain that the ferrous oxide contained in the ferrous oxalate reduces the silver oxide in the silver salt to the state of metallic silver.

$$\underset{\text{Ferrous Oxide}}{2FeO} \quad \underset{\textit{and}}{+} \quad \underset{\text{Silver Oxide}}{Ag_2O} \quad \underset{\textit{produce}}{=} \quad \underset{\text{Silver}}{2Ag} \quad \underset{\textit{and}}{+} \quad \underset{\text{Ferric Oxide}}{Fe_2O_3}$$

The object of the citrate of soda in this and in the washing solutions is to prevent the precipitation of the iron by the ammonia used for dissolving the silver salts.

It now only remains to wash everything out of the paper except the black metallic silver which forms the picture. This is effected by soaking the print for ten minutes in each of the following three solutions:

WASHING SOLUTION NO. 1.

Kallitype developer	½ ounce
Citrate of soda (pure, neutral)	2 ounces
Water	20 ounces

WASHING SOLUTION FOR BATHS NOS. 2 AND 3.

Citrate of soda (pure, neutral)	1 drachm
Ammonia (.880)	2 drachms
Water	1 quart

These two baths must always smell distinctly of ammonia.

Finally the prints are rinsed in several changes of water and then dried.

All the solutions can be bottled and used over and over again. The paper was sold by the Birmingham Photographic Co., Gladstone Road, Birmingham, at ten pence per sheet (26 x 20 inches), so that the process was a cheap one. It gives prints of brown or black tones, not unlike bromide paper or platinotype; and as no hypo is employed for fixing, the prints should be more permanent than ordinary silver prints.

The printing under the negative must be carried on until a faint brown image is visible, just showing the details under the densest parts; this only requires about ten minutes in diffused light, or two minutes in sunshine. After floating on the developing solution, it is a good plan to lay the prints, face upward, on a sheet of clean glass for a minute or two, when they will gain in brilliancy and in depth.

Kallitype No. II.

In 1891 Dr. Nicol improved his kallitype printing process by putting the silver salt *in the paper*. The new paper is coated with two iron salts—ferric oxalate and ferric nitrate—and also with the corresponding two silver salts—silver oxalate and silver nitrate. By exposure to light the ferric oxalate is reduced to the ferrous state.

The print is then developed by floating upon the following bath:

Rochelle salt ($NaKC_4H_4O_6$)	1 ounce
Borax	¾ ounce
Water	10 ounces

Add to this 10 drops of a solution of bichromate of potash. (Strength, 20 grains to 1 ounce.)

This gives black tones, which can be changed to purple by diminishing the borax to one-quarter of an ounce.

The ferrous oxalate combines with the Rochelle salt, and reduces the silver to the metallic state; the Rochelle salt also combines with the iron to form ferric tartrate—$Fe_2(C_4H_4O_6)_3$.

The prints should be left in the developing bath for at least twenty minutes. They are then removed and fixed by immersion in two baths of water to which ammonia has been added in the proportion of four drachms to every quart.

CHAPTER XXVII.

THE PLATINOTYPE PRINTING PROCESS AND ITS CHEMISTRY.

Certain compounds containing platinum have long been known to be somewhat sensitive to light; but it may be at once said that in the platinotype process the effect of light upon platinum compounds may be altogether neglected. The process is, in fact, an indirect one. We get the light to act upon a certain salt of iron, which is mixed with a platinum salt, and then the altered iron salt is caused to act *chemically* upon the platinum salt.

A *permanent* printing process has always been a great desideratum in photography. No "silver print" can be considered permanent; although there are "exceptions which prove the rule," yet it is a well-known fact that the great majority of ordinary photographs printed in silver—upon glossy albumenized paper—deteriorate steadily from the time of their production until they become yellow and faint, perhaps even disappearing altogether.

Now there are two substances known to the chemist, whose permanence he regards as "beyond reproach"; these are carbon and platinum.

The carbon process has been practised since 1858, and will be treated of separately. Platinum had also been used to "tone" prints, etc., but until William Willis, Jr., announced his results in 1873, no one had succeeded in obtaining a good photographic print in metallic platinum. Willis improved his process, and took out further patents in 1878, 1880, and later years. We shall not follow all the steps which led Willis to a final and great success, but will describe, from a chemical point of view, the perfected platinotype process as now practised. In England, at all events, platinotype is now the process employed by the majority of the best workers when they wish to obtain the best results.

Table of the Platinotype Processes, Showing the Various Modifications.

Hot-Bath Platinotype, Willis, 1873 (perfected 1880).
Cold-Bath Platinotype, No. I., Willis, 1888.
Printing-Out Platinotype, Pizzighelli, 1888.
Cold-Bath Platinotype, No. II., Willis, 1892.

Platinum forms two series of compounds with the non-metallic elements. Thus, taking chlorine as a type of the non-metals, we have Platinic Chloride, $Pt\,Cl_4$; and Platinous Chloride, $Pt\,Cl_2$. Willis reasoned that it would be better to employ the latter or *-ous* series, since there would be less work to be done in separating platinum from *two* atoms of chlorine than from *four* atoms. This was the first element in his success. The experimenters before him had used the higher or *-ic* series.

Willis' second discovery was that when ferrous oxalate is dissolved in neutral potash oxalate it is able to instantly reduce to the metallic state the platinous salts mentioned above.

Now *ferrous* oxalate is produced whenever *ferric* oxalate is exposed to light, the change which takes place being expressed chemically as follows:

$$\underset{\text{Ferric oxalate}}{Fe_2(C_2O_4)_3} \quad \underset{\textit{becomes}}{=} \quad \underset{\text{Ferrous oxalate}}{2Fe(C_2O_4)} \quad \underset{\textit{and}}{+} \quad \underset{\text{Carbonic acid gas.}}{2CO_2}$$

Coat some paper with a solution of ferric oxalate (100 grains to the ounce of water); dry, and expose to light beneath a negative. A brownish image will be formed, which consists of ferrous oxalate. By itself this image is of no use, but it can be used to produce an image in metallic platinum.

Select some strong, smooth white paper (the best kind of drawing-paper, for example). Size this paper by dipping it into a weak solution of gelatine (150 grains to the ounce of water), the object of the sizing being to prevent the chemicals with which the paper is to be coated from sinking too deeply into its substance.

THE HOT-BATH PLATINOTYPE PROCESS.

For coating the paper two solutions must be prepared:

1.	Ferric oxalate	120 grains
	Oxalic acid (crystallized)	6 grains
	Water (distilled)	1 ounce
2.	Chloro-platinite of potassium solution.	

This second solution is made by dissolving eighty grains of the salt in one ounce of distilled water.

The sensitizing solution is made up as follows:

No. 1	22 fluid drachms
No. 2	24 fluid drachms
Distilled water	4 fluid drachms

This sensitizing solution must be made up as wanted, and must be kept from the light.

Now take the dry sized paper and fold its edges over a sheet of glass of nearly the same size, or pin it down upon a smooth board, so as to secure a flat surface. For an ordinary sheet of paper—say, 22 x 17 inches—2½ drachms of the sensitizing solution should be poured on the middle of the paper and quickly spread all over it by rubbing gently with a pad of cotton-wool. This should be done in a weak white light, as (the solution being of a yellow color) it is otherwise difficult to see if the paper is properly coated.

Now hang up the sheet by its corners, and allow it to become just surface-dry. This ought to take not less than five, nor more than ten minutes. Lastly, thoroughly dry the paper by means of a clear fire or gas-stove.

Paper so prepared will keep good for months if it be kept perfectly dry. This can only be insured by keeping the paper (rolled up, with surface side out) in a tin tube, which also contains calcium chloride wrapped up in a little cotton-wool and muslin. The latter chemical absorbs all the moisture from the air in the tube.

Printing is done in a frame, in the ordinary way, but it is best to lay a piece of sheet india-rubber at the back of the paper, in order to prevent the access of moisture. Almost the only difficulty of the platinotype process (hot or cold bath) is to tell when the printing is complete. As a rule, it may be said that *all but the faintest details* should be visible in the faint greenish-brown image (which consists of ferrous oxalate, be it remembered) which is seen when one flap of the printing frame is turned back, and the side of the paper in contact with the negative examined.

It now remains to convert this weak "iron" image into a vigorous image in "platinum black."

Make a saturated solution by dissolving 16 ounces of neutral potash oxalate in 54 ounces of hot distilled water. Place this in an enamelled iron dish, and heat it to a temperature of 150 deg. F., as indicated by a thermometer immersed in the liquid.

Now float the exposed prints one at a time for six seconds each upon this hot solution. Instantly the picture appears; and, if all has been well and the negative is a good one, we obtain an exquisite engraving-like picture, in which the gradations will (in the finished print) range from soft velvety blacks to pure whites.

The chemical change or reaction which takes place is a most beautiful one, and may be expressed as follows:

$$\underset{\text{Ferrous Oxalate}}{6\,\mathrm{Fe\,C_2O_4}} \underset{\textit{and}}{+} \underset{\substack{\text{Chloro-platinite}\\ \text{of Potassium}}}{3\,\mathrm{K_2\,Pt\,Cl_4}} \underset{\textit{produce}}{=} \underset{\text{Platinum}}{3\mathrm{Pt}} \underset{\textit{and}}{+} \underset{\substack{\text{Ferric}\\ \text{Chloride}}}{\mathrm{Fe_2Cl_6}} \underset{\textit{and}}{+} \underset{\text{Ferric Oxalate}}{2\mathrm{Fe_2(C_2O_4)_3}} \underset{\textit{and}}{+} \underset{\substack{\text{Potassium}\\ \text{Chloride}}}{6\mathrm{K\,Cl}}$$

The moment the ferrous oxalate touches the hot potash oxalate it is dissolved, and it then attacks the potassium salt, decomposing it and producing metallic platinum, which is deposited on the paper and forms the new picture.

It will be seen that a quantity of iron salts also remains in the paper. These discolor the paper, and they must be removed by soaking the developed prints in two or three changes of dilute hydrochloric acid (one ounce of the acid to sixty of water).

Finally the prints are washed for half an hour in running water, and are then dried between blotting-paper.

Over or under-exposure can be corrected to some extent by the use of a cooler (100 deg. Fahr.) or hotter (200 deg. Fahr.) bath.

By the addition of a few drops of a saturated solution of mercury bichloride to the developing bath, prints of a sepia tone can be obtained.

THE COLD-BATH PLATINOTYPE PROCESS.

No. I.

In this form of platinotype, the paper is coated with a solution containing 120 grains of ferric oxalate and one grain of mercury bichloride to the ounce of water. It is thoroughly dried, exposed to light beneath a negative, and then floated on a cold solution containing fifty grains of potash oxalate and ten grains of chloro-platinite of potassium to each ounce of water. The paper should at once be lifted up from the cold solution and laid face upwards on a glass plate. Development proceeds slowly, and can be stopped when desired. Or the cold solution may be applied to the paper with a brush if desired. The mercuric salt acts by increasing the reducing power of the ferrous oxalate. The prints require clearing with acid, and then washing, as in the hot process.

No. II.

At the Camera Club Conference in March, 1892, Mr. Willis announced what appears to be the crowning improvement of the platinotype process. By a certain modification of the ordinary hot-bath method the developer can be used *cold*, *i.e.*, at ordinary temperatures. The image ought to be printed-out rather more than when the hot-bath is employed. No details were given as the patent was not completed, but the new paper has since been placed upon the market and has given the greatest satisfaction. By mixing the developer (ordinary potash oxalate solution) with glycerine, and applying it with a brush, the process is so far under control that great variations can be made in the results, and very artistic effects produced.

PIZZIGHELLI, OR PRINTING-OUT PLATINOTYPE.

The hot process might be called the "platinum in the paper" method, as distinguished from the cold process, No. I., in which we have the "platinum in the bath." But in the method devised by the Austrian experimenter, Pizzighelli, we do away with the bath altogether, and put all the substances employed, developer and all, upon the paper.

Make up the following solutions:

a	Chloro-platinite of potassium	60 grains
	Distilled water	1 ounce
b	Sodium oxalate	15 grains
	Sodium-ferric oxalate	3 drachms
	Chlorate of potash	1 grain
	Distilled water	1 ounce

To sensitize a sheet of paper (22 x 17 inches) mix two drachms of *a* with two drachms of *b*, and apply to the (previously well-sized) paper as described above.

The prepared paper is printed right out in the printing-frame, exactly like silver paper, and to just the depth required. It is then cleared with acid (1 to 80) and washed as before. It will be found advantageous to slightly damp the paper just before using, either by breathing upon it, or by passing it over a pan-full of hot water. The chemical changes which take place are practically the same as those given under the hot-bath process; the moisture which is necessary to development is obtained by the paper absorbing it from the air.

The advantages of this "printing-out" method are fewer spoilt prints; and the power of inserting clouds with greater ease. Its disadvantages, the fact that the blacks are not nearly so vigorous, and that it takes much longer to print (about twice as long as silver paper); while for the hot or cold-bath processes the time required for printing is less than half that needed for silver paper.

Mr. Willis' patents are worked in England by the Platinotype Co., 29 Southampton Row, High Holborn, London*; and his American representatives are, we believe, Willis &

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* They issue pamphlet of instructions, which is well worth writing for.

Clements, of Philadelphia; but all the materials we have named can be obtained through the Scovill & Adams Co., 423 Broome Street, New York City. The preparation of the paper for the hot process is the easiest thing possible, and we recommend all who desire the very best results possible to sensitize their own paper. The Pizzighelli paper is made, we believe, only in Vienna, but it can be obtained to order through any dealer.

To show the rate at which the platinotype process is spreading in England, we may say that at the exhibition held in Pall Mall in November, 1889, out of 639 frames exhibited no fewer than 205 were occupied by platinotypes. Of these 183 were by the hot bath; 3 by the cold bath; and 19 by the Pizzighelli process.

Platinum Toning.

This article would scarcely be complete without some reference to a process of toning silver prints with platinum, introduced in 1889 by Mr. Lyonel Clark. Mr. Valentine Blanchard had previously sold prepared paper and solutions for the same or a very similar process, but he did not publish his method.

All platinum printing processes at present known are *substitution* processes. A "provisional" image is formed in some other metal, and then—by a chemical change—platinum is caused to replace the metal. In Willis' platinotype the provisional image is in iron; but, as Mr. Clark points out, silver will also answer the purpose.

Plain or matt-surface paper must be employed, because albumen prevents the free replacement of the silver by the platinum. Such matt-surface paper, ready sensitized, can now be bought of most dealers; or it can be prepared in the following way. Make up these solutions:

A—Salting Solution.

Gelatine	90 grains
Ammonium chloride	60 grains
Carbonate of soda (recrystallized)	120 grains
Citric acid (crystals)	30 grains
Distilled water	10 ounces

On this solution float any good, strong white paper, and pin the sheets up till dry.

B—Sensitizing Solution.

Silver nitrate	90 grains
Distilled water	1 ounce

This solution must be kept in a bottle, round which two or three layers of brown paper have been pasted to protect it from the light.

It is now only necessary to float the salted paper upon solution *B* (of which ten or twenty ounces may be made up); or, if only a small quantity of paper is to be sensitized, the solution may be applied with a brush or a glass rod. But the paper once sensitized will not keep for more than two or three days.

Prints are to be made on this matt-surface paper in the usual way; and they should be printed rather dark, for the subsequent toning with platinum will somewhat reduce them.

The platinum toning-bath is made up as follows:

Chloro-platinite of potassium	30 grains
Water	30 ounces
Nitric acid	10 drops

The silver prints must be immersed in this bath (if only a few at a time are done, they can be floated face down on a little of the platinum solution poured into a levelled dish), and their reddish tint changes first to brown and then to black; only two or three prints should be in the bath at the same time. The chemical change which takes place may be represented by the following equation:

$$\underset{\text{Silver}}{2Ag} \underset{\textit{with}}{+} \underset{\substack{\text{Chloro-platinite}\\\text{of Potassium}}}{K_2PtCl_4} \underset{\textit{produces}}{=} \underset{\text{Platinum}}{Pt} \underset{\textit{and}}{+} \underset{\substack{\text{Silver}\\\text{Chloride}}}{2AgCl} \underset{\textit{and}}{+} \underset{\substack{\text{Potassium}\\\text{Chloride.}}}{2KCl}$$

When the desired tone has been attained, the prints must be well rinsed in water, to which a little ammonia has been added. They are then placed in a fixing-bath (hypo, four ounces, to twenty of water) for twenty minutes; and are finally well washed for several hours in plain water.

Compared with platinotypes proper, these "platinum-toned" prints can hardly claim equal probability of permanency; but they are more permanent than the ordinary "gold toned" silver prints, over which they possess further advantages in their fine black tones and matt-surface.

In conclusion, platinum printing processes are no longer "in the future"; they are firmly established, and are gaining ground every day. The treacherous silver prints on albumenized paper—despised by every artist—will soon become things of the past, and a great reproach will be wiped away from photography.

APPENDIX.

LITERATURE OF PLATINUM PRINTING PROCESSES.

JOURNAL OF THE PHOTOGRAPHIC SOCIETY OF GREAT BRITAIN:

W. Willis, Jr.—Notes on the Platinotype Process, N. S., Vol. III. (for 1878), p. 32.

Spiller, J.—The Fading of Platinotype Prints, N. S., Volume III., p. 74.

Abney, Capt.—On Platinotype Deposits, N. S., Vol. XII. (for 1888), p. 165.

Platinotype.—By *Capt. Pizzighelli* and *Baron A. Hubl;* translated from the German by J. F. Iselin and edited by Capt. Abney; published by Harrison & Sons, 59 Pall Mall, London; price, two shillings.

PROCEEDINGS OF THE (LONDON) CAMERA CLUB.

H. H. O'Farrell.—Sulphuration of Platinotype Prints, Vol. I. (for 1887), p. 41.

W. Willis.—A Recent Improvement in Platinotype (Cold Development), Vol. II.. (for 1888), p. 47.

W. Willis.—Platinotype (Hot) Printing Process, Vol. II., p. 99.

W. Willis.—Platinotype (Cold) Printing Process; Vol. II., p. 103.

Blanchard, Valentine.—Platinum Toning Process, Vol. II., p. 128.

Cembrano, Stroh, Dresser, etc.—Opinions on the Pizzighelli (Printing-out) Platinotype Process, Vol. II., pp. 136, 147.

Cembrano, F. de P.—Printing-out Platinotype; and a Comparison of Platinotype Processes, Vol. II., p. 153.

Willis, W.—A Lesson on the Cold-Bath Process, Vol. II., p. 170.

Clark, Lyonel.—A New Platinum Toning Process, Vol. II., p. 185.

Willis, W.—Recent Improvements in Platinotype, Vol. VI., pp. 53, 119.

British Journal of Photography.

Pizzighelli, Capt. G.—The Direct Production of Platinotypes in the Printing Frame Without Development, Vol. XXXV. (for 1888), pp. 213, 230.

Cunningham, H. H.—The New Platinotype Cold Development Process, Vol. XXXV., p. 552.

Bedding, T.—The New (Pizzighelli) Platinum Process, Vol. XXXV., p. 566.

Fox, N. P.—Platinotype Printing, Vol. XXXVI. (for 1889), p. 333.

Beach, F. C.—The Pizzighelli Platinotype Paper, Vol. XXXVI., p. 538.

Beetham, W. C.—Platinotype Printing, p. 21 (for 1890).

Pike, John.—The Platinotype Process, p. 759 (for 1890).

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CHAPTER XXVIII.

REDUCING PROCESSES AND THEIR CHEMISTRY.

Meaning of the Term "Reduction."—As used in photography, the word "reduction" has three distinct meanings. It may mean reduction in size, or reduction to the metallic state, or reduction in density. It is in the latter sense that the term is used here. In chemistry the word *reduction* is used in a totally different sense, and is taken as the equivalent of "deoxidation," or the removing of oxygen from a compound. To avoid all confusion, some writers on photography prefer to substitute "weakening" for "reducing." For reducing agents *weaken* the image and render it less dense.

Necessity for Reduction.—During the development of a negative in the dim light of the photographer's dark-room it is very easy to make the mistake of developing the negative *too much.* After fixing, the negative then presents a black and nearly opaque appearance. It prints badly, and so slowly that days of exposure to sunlight sometimes fail to produce the desired effect.

The same thing may happen in the production of positives upon glass (transparencies or lantern-slides); also in the production of developed prints (bromides or platinotypes), or even in the case of ordinary silver prints.

The remedy—partial or complete—in all these cases is *reduction.* It may be that the negative, etc., is too dense in certain parts only; we must then resort to *local* reduction.

Reduction Easier than Intensification.—It is generally acknowledged that the most difficult point in development is to know exactly *when to stop.* On the whole, it is better to over-develop rather than to stop development too soon. In the latter case, not only may density be wanting, but all the detail may not have been got out. It is found, too, that better results are obtained from a negative which has been reduced than from one that has been intensified.

What Hardwich Meant by "Reduction."—In all the nine editions of Hardwich's "Manual of Photographic Chemistry" (1855–83) he uses the term "reduction" in its chemical sense. As he points out clearly enough, a developing agent is—chemically speaking—a "reducing" agent; that is, it causes a separation of some metal—almost invariably *silver*—from the non-metallic element or elements with which it may be combined; and this "reduced" silver then composes the photographic image or picture.

Thus Hardwich's reduction is not *our* reduction. Nor have we been able to find in his once-popular and largely-read book any term which is equivalent to *reduction* when it means the lessening of the density of a negative, etc.

We can only explain this by remembering that the *need* for such a method was not anything like so great with collodion as with gelatine. The worker with collodion *built up* his picture by the aid of plenty of yellow light, and by the addition of silver to the developer. He could tell exactly when to stop. Moreover, the collodion negative was, as a rule, developed at the time and at the place when and where it was taken. And if the negative did not turn out well, it was cleaned off the glass and another exposure made. The wet-collodion worker *knew what he was taking home.*

The text-books of Hunt, Lake-Price, etc., contemporary with the earlier editions of Hardwich, agree with that author in neglecting to treat of reduction.

"Reduction" of Residues.—Another example of the use of the term "reduction," in its *chemical* sense, is the way in which it is universally applied to the converting of photographers' residues (which contain gold, silver, etc.) to the metallic state. Perhaps some future photographic congress will issue a revised nomenclature of words employed technically in our art, so that each term shall have a fixed and definite meaning.

Reduction Processes Used in Collodion Times.—Still, the photographic periodicals of the wet-collodion times (1853–79) show us that reduction was not uncommonly practised, at all events during the latter half of that epoch. One favorite reducer appears to have been a solution of iodine with iodide of potassium and cyanide of potassium. The iodine attacked the image, converting some of its silver into silver iodide; and this was then dissolved away by the cyanide.

Mr. R. Kennett gave the following formula in 1879:* "Take cyanide of potassium, 10 grains; water, 1 ounce; to this add crystals of iodine as long as any will dissolve. With a camel-hair brush paint this over the parts to be reduced. Then wash well and dry."

Mr. Stillman states † that the same reducer is good for gelatine films. He writes: "I put enough of the usual solution of iodine with iodide of potassium, with the quantity of water required to flood the plate copiously, to give it a good port-wine color, and then add a concentrated solution of cyanide of potassium until the color disappears and is replaced by opalescence." The plate to be reduced is soaked in water and then placed in the above solution till reduced. The dish must be rocked frequently. Mr. Stillman adds: "I have reduced a plate over-intensified by carelessness in the mercury solution until it had become perfectly orange and imprintable, without stain or marking, or losing the most delicate detail. But the plate must be carefully washed between all the operations, and leave no trace of the hypo in the film."

Ferric Chloride as a Reducer.—When a solution of ferric chloride or "chloride of iron" is poured upon a negative, it combines with the silver of the image to form silver chloride, which, being white and translucent, lowers the density considerably. The action which takes place may be represented by a chemical equation:

$$\underset{\text{Silver}}{Ag_2} \;\; \textit{and} \;\; \underset{\text{Ferric Chloride}}{Fe_2Cl_6} \;\; \textit{produce} \;\; \underset{\text{Silver Chloride}}{2AgCl} \;\; \textit{and} \;\; \underset{\text{Ferrous Chloride.}}{2FeCl_2}$$

$$Ag_2 + Fe_2Cl_6 = 2AgCl + 2FeCl_2$$

The silver chloride must be removed by placing the (washed) negative in an ordinary fixing bath of hypo, and the negative is then to be finally washed and dried.

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* "Photo News Year Book," p. 67.

† "British Journal Almanac," 1883, p. 142.

The difficulty in this method is to know exactly when to remove the negative from the ferric-chloride bath. The best plan is to use a glass dish, and watch the reduction carefully by the aid of light reflected upward through the bottom of the dish from a looking-glass placed at an angle beneath.

The strength of the solution of ferric chloride is not very material; it should be of the color of sherry wine, which may be produced by adding four grains of the solid chloride to every ounce of water. Two or three drops of hydrochloric acid to each ounce of water is also an improvement. About five minutes in this solution will be sufficient to effect a moderate reduction, followed by ten minutes in ordinary hypo solution. If the reduction is not found sufficient, the negative must be well washed and the process repeated. The method is also useful for clearing yellow stains, etc., from negatives and for removing surface fog.

Decolorizing Negatives Reduced by Ferric Chloride.—The ferric chloride reducer too frequently leaves a yellow stain behind. M. E. Audra[*] removes this in the following way: To a 10 per cent. solution of sulphite of soda in water add sulphuric acid, drop by drop, until there is a distinct smell of sulphurous acid. Immerse the stained negative in this solution, by which it will speedily be cleared. This is stated to be also a good clearing agent for pyro stains.

Ferric Sulphate (persulphate of iron) as a Reducer.—A solution of ferric sulphate in water, of the strength of three grains to the ounce, acts as a powerful reducer. Its use for this purpose was described by Professor Vogel in 1886. The sulphate dissolves but slowly in water, so it should be stirred well with a glass rod and allowed to stand for half an hour before using.

The chemical reaction is:

$$Ag_2 + Fe_2(SO_4)_3 = Ag_2SO_4 + 2FeSO_4$$

Silver *and* Ferric Sulphate *produce* Silver Sulphate *and* Ferrous Sulphate.

The silver sulphate dissolves slowly in the water as it is produced; but the negative should afterwards be soaked for ten minutes in a weak hypo fixing bath, which rapidly dissolves the silver sulphate. Afterwards wash and dry.

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[*] "British Journal Almanac," for 1884, p. 48.

Copper Chloride as a Reducer.—Chloride of copper—or cupric chloride, as it is more correctly called—acts in exactly the same way as ferric chloride. It combines with the silver of the negative to form silver chloride:

$Ag_2 + 2CuCl_2 = 2AgCl + Cu_2Cl_2$
Silver *and* Cupric Chloride *produce* Silver Chloride *and* Cuprous Chloride.

The negative must then be immersed in the ordinary hypo fixing bath to remove the silver chloride. After washing, it should be soaked in an acid and alum clearing bath, which will remove the cuprous chloride. It must then be finally washed and dried.

The reducing solution may be made up of three grains of solid copper chloride to every ounce of water. It should be of a pale blue color.

Where the copper chloride is not at hand, it can be *made* by mixing 4 grains of copper sulphate and 6 grains of sodium chloride to 1 ounce of water.

$CuSO_4 + 2NaCl = CuCl_2 +$
Copper Sulphate *and* Sodium Chloride *produce* Cupric Chloride *and*
Na_2SO_4
Sodium Sulphate.

The mixture can be used for reducing just as it is, as the presence of the sodium sulphate makes no difference.

Spiller's Reducer.—Mr. Spiller recommends the following form of the copper chloride reducer. Make up two stock solutions:

A.—Alum	4 ounces
Copper sulphate (bluestone)	4 ounces
Common salt	8 ounces
Water	1 quart

B.—A saturated and filtered solution of common salt.

Mix these two solutions in equal parts—say, 3 ounces of each—and immerse the negative in the mixture. If the negative is very dense, 4 or 5 ounces of B may be used to 3 of A. When reduction has been effected, soak for ten minutes in B alone; then wash with plain water and dry.

The chemical action may be expressed in a single equation:

$2CuSo_4 \quad + \quad 4NaCl \quad + \quad Ag_2 \quad =$

Copper Sulphate *and* Sodium Chloride *and* Silver *produce*

$2AgCl \quad + \quad 2Na_2SO_4 \quad + \quad Cu_2Cl_2$

Silver Chloride *and* Sodium Sulphate *and* Cuprous Chloride.

The cuprous chloride and the silver chloride are both dissolved by the (B) solution of common salt.

Copper Sulphate as a Reducer.—Dissolve half an ounce of copper sulphate in a pint of water. Add ammonia, drop by drop, until the precipitate which is first formed just disappears.

Make a solution of 1 ounce of hyposulphite of soda in 10 ounces of water. Soak in this the negative to be reduced. Add a few drops of the copper sulphate solution and soak well; add more copper as required. Afterwards wash well and dry.

$Ag_2 \quad + \quad Cu(NH_3)_2(SO_4)_2 \quad + \quad 2H_2O \quad =$

Silver *and* Ammonia-Sulphate of Copper *and* Water *produce*

$Ag_2SO_4 \quad + \quad CuH_2O_2 \quad + \quad (NH_4)_2SO_4$

Silver Sulphate *and* Copper Hydrate *and* Ammonium Sulphate.

The chemical action may be represented by the above equation. Silver sulphate is formed, and then this is dissolved away by the hypo solution.

"Ozone Bleach" and other Hypochlorites as Reducers.—The substance known as "Holmes' Ozone Bleach" was at one time much used (its price was only eight-pence per quart bottle) for laundry work and as a disinfectant. Chemically it is sodium hypochlorite. It was recommended by Mr. W. E. Debenham as a reducer in 1881; and he gave the following formula in 1882:

Ozone bleach	½ ounce
Chrome alum	10 grains
Water	5 ounces

The negative to be reduced is soaked in the above solution for a few minutes, during which time part of the image is converted into silver chloride according to the following equation:

$$\begin{array}{cccccccc} \mathrm{Ag_2} & + & \mathrm{2NaOCl} & + & \mathrm{H_2O} & = & \mathrm{2AgCl} & + \\ \text{Silver} & \textit{and} & \text{Sodium Hypochlorite} & \textit{and} & \text{Water} & \textit{produce} & \text{Silver Chloride} & \textit{and} \end{array}$$

$$\begin{array}{ccc} \mathrm{2NaHO} & + & \mathrm{O} \\ \text{Sodium Hydrate} & \textit{and} & \text{Oxygen} \end{array}$$

The negative is then dipped into hypo, which removes the silver chloride, and the image is thus "reduced."

The object of the chrome alum is to harden the gelatine. If it is dispensed with, the hypochlorite attacks both the gelatine and the silver, and the surface of the film is converted into a slimy layer which should be rubbed off with a pad of cotton-wool. Some have preferred to use this reducer in this fashion; but the addition of the chrome alum brings the reduction more under control.

Other Hypochlorites act in a like manner to "ozone bleach"; and since the latter appears to be not now readily obtainable, they may be used instead of it with identical results. Thus we have Robinson's method * of mixing hypochlorite of sodium (two parts of the commercial solution) with one part of a saturated solution of alum. Filter; and then bottle for use. Robinson gives the following equation:

$$\begin{array}{ccccc} \mathrm{2AlK(SO_4)_2} & + & \mathrm{6NaClO} & + & \mathrm{6H_2O} \\ \text{Alum} & \textit{and} & \text{Sodium Hypochlorite} & \textit{and} & \text{Water} \\ = & \mathrm{Al_2H_6O_6} & + & \mathrm{3Na_2SO_4} & \\ \textit{produce} & \text{Aluminium Hydrate} & \textit{and} & \text{Sodium Sulphate} & \\ + & \mathrm{K_2SO_4} & + & \mathrm{6HClO} & \\ \textit{and} & \text{Potassium Sulphate} & \textit{and} & \text{Hypochlorous Acid} & \end{array}$$

When the solution is poured upon a negative, the hypochlorous acid combines with the silver of the image to form silver chloride, which can afterwards be removed by a bath of ordinary hypo.

$$\begin{array}{ccccc} \mathrm{Ag_2} & + & \mathrm{2HClO} & = & \mathrm{2AgCl} \\ \text{Silver} & \textit{and} & \text{Hypochlorous Acid} & \textit{produce} & \text{Silver Chloride} \\ & + & \mathrm{H_2O} & + & \mathrm{O} \\ & \textit{and} & \text{Water} & \textit{and} & \text{Oxygen} \end{array}$$

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* *Photographic News*, 1887, p. 499.

Of the bottled solution as described, one part should be mixed with three parts of water for use.

The negative should be removed from the reducing solution a little *before* the reduction required has been obtained; since the action will continue for some time while the reducer is in course of being washed out, and also because the removal of the silver chloride by the hypo causes a slight further loss of density.

Reduction with "Bleaching Powder."—Ordinary bleaching powder is calcium hypochlorite. It may be dissolved in water in the proportion of 20 grains to the ounce, and filtered; and will then reduce any negative which may be soaked in it.

The action is as follows:

$$\underset{\text{Calcium Hypochlorite}}{CaCl_2O_2} \underset{\textit{and}}{+} \underset{\text{Silver}}{Ag_2} \underset{\textit{produce}}{=} \underset{\text{Silver Chloride}}{2AgCl} \underset{\textit{and}}{+}$$

$$\underset{\text{Calcium Oxide}}{CaO} \underset{\textit{and}}{+} \underset{\text{Oxygen}}{O}$$

The negative must then be *well rinsed*, soaked in a bath of hypo (to remove the silver chloride), washed and dried.

Great care must be taken in using this method, or the gelatine will be so softened that the film will come away.

This reducer was described in the "Photo News Year-Book" for 1886, p. 37, by Mr. R. W. Robinson. He points out that the negative must be previously thoroughly *dried*, and that the reduction must be stopped as soon as the film begins to feel slimy. Local reduction can be effected by gentle rubbing with the finger on the part desired.

Eau de Javelle as a Reducer.—The liquid known as "eau de javelle" is sold commercially, and a good reducer may thus be made:

Eau de javelle	1 ounce
Chrome alum	25 grains
Water	10 ounces

Dissolve the alum in the water, and then add the eau de javelle. The mixture is at first green and turbid, but becomes a clear yellow in a few minutes.

The negative must be soaked, first in water, and then in the above solution till reduced. Finally, wash well, fix in ordinary hypo, wash again, and dry.

Where eau de javelle cannot be purchased, a reducing solution containing it can be made up as follows:

Dry chloride of lime	2 ounces
Carbonate of potash	4 ounces
Water	30 ounces

Dissolve the lime in 20 ounces of the water, and the potash in the remaining 10 ounces. Mix, boil, and filter. This is the reducing solution in which the negative is to be immersed. The subsequent operations are the same as those described above.

Reducing with Condy's Fluid.—Mr. W. C. Williams gave the following method in 1881:*

Condy's fluid	½ dram
Saturated solution of alum	4 ounces

Condy's fluid is a solution of permanganate of potash; and instead of buying the bottled "fluid," the solid permanganate may be dissolved in water in the proportion of 2 grains per ounce.

The negative is to be soaked in the mixture for ten or fifteen minutes, then washed, soaked in ordinary hypo solution, well washed, and finally dried. We find that this method stains the negative yellow or red, and we do not recommend it, although it certainly reduces the image effectually enough.

Reducing with Bichromate of Potash.—Make up the following solution:

Bichromate of potash	2 parts
Sulphuric acid	4 parts
Water	100 parts

Soak the dried negative in the water for an hour, and then immerse in the above solution. Watch its action carefully, as it reduces quickly. This method was recommended by Mr. W. Hanson in the *British Journal of Photography* for February 23, 1872.

Farmer's Ferridcyanide Reducer.—The most "popular" reducer of the present day is probably that first recommended in 1883 by Mr. Howard Farmer (instructor in photography at the Polytechnic Institution, London), and described by him in detail in the "Photo News Year-Book" for 1884. Make up the following solutions:

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* *British Journal of Photography*, Vol. XXVIII, p. 29.

A.—Ferridcyanide of potassium		1 ounce
	Water	1 pint
B.—Hyposulphite of soda		1 ounce
	Water	1 pint

Soak the negative in the hypo solution for a few minutes, and then pour off the hypo into a glass vessel. Add to the hypo a few drops of the ferridcyanide solution (enough to make it sherry colored), and pour the mixture over the negative. Gradual reduction will take place. When the action stops add a few more drops of the ferridcyanide if the reduction is not sufficient. Then remove the negative, wash well, and dry. The operation is best performed in a weak light. The mixed solutions do not keep.

Ferridcyanide (or *ferricyanide*) of potassium is commonly called red prussiate of potash. It combines with the silver of the image to form silver ferrocyanide, and then this is dissolved away by the hypo, the negative thus becoming thinner and thinner. The first action is expressed by the equation:

$2Ag_2$ + $2K_6Fe_2(CN)_{12}$ = $Ag_4Fe(CN)_6$
Silver *and* Potassium Ferridcyanide *produce* Silver Ferrocyanide
+ $3K_4Fe(CN)_6$
and Potassium Ferrocyanide.

The hypo then acts as follows:

$Ag_4Fe(CN)_6$ + $4Na_2S_2O_3$ =
Silver Ferrocyanide *and* Sodium Hyposulphite *produce*
$4AgNaS_2O_3$ + $Na_4Fe(CN)_6$
Silver Sodium Hyposulphite *and* Sodium Iron Ferricyanide.

As the two chemical actions take place simultaneously, the reduction can be seen as it progresses and arrested at any moment. This is one of the best points of the process. The mixture, however, does not keep well, so that it cannot be prepared and bottled for use, but must be made as required, As stated in another paragraph, this method can also be used for reducing silver prints.

Belitzki's Ferric Oxalate Reducer.—The following reducer is due to Herr L. Belitzki, of Nordhausen.

Make up the following solution:

A.—Ferric chloride	10	grains
Potash oxalate	½	ounce
Water	1½	ounce

Chemical combination will take place and ferric oxalate will be formed, as shown by the equation:

Fe_2Cl_6 + $3K_2C_2O_4$ = $Fe_2(C_2O_4)_3$ +
Ferric Chloride *and* Potash Oxalate *produce* Ferric Oxalate *and*
$6KCl$
Potassium Chloride.

The ferric oxalate so formed is ready to act as our reducer; but we must also have some substance present which will dissolve or wash off the silver oxalate which will be formed. Such a substance is found in sodium hyposulphite. Make up, therefore, a second solution as follows:

B.—Hypo	½	ounce
Water	2	ounces

Mix this with solution A, as given above.

When the negative to be reduced* is placed in the mixed solutions A and B, the ferric oxalate at once combines with the silver of the image to form silver oxalate.

Ag_2 + $Fe_2(C_2O_4)_3$ = $Ag_2C_2O_4$ +
Silver *and* Ferric Oxalate *produce* Silver Oxalate *and*
$2FeC_2O_4$
Iron Oxalate.

Then the hypo combines with the silver oxalate to form a soluble salt, which is washed off by the water.

$Ag_2C_2O_4$ + $2Na_2S_2O_3$ =
Silver Oxalate *and* Sodium Hyposulphite *produce*
$2AgNaS_2O_3$ + $Na_2C_2O_4$
Silver Sodium Hyposulphite *and* Sodium Oxalate.

The negative must be carefully watched while in the reduc-

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[*] If the negative has been dried it should be well washed before reducing.

ing solution, so that it may not be made too weak. The action is, however, very steady and gradual. Occasionally the plate may be lifted out and examined by transmitted light.

The negative is finally well washed and dried. This method of reduction has been approved by that high authority, Dr. Eder, and is sometimes known as "Eder's" reducer.

A Reducer Contained in Used Ferrous Oxalate.—Instead of the mixture of ferric chloride and potash oxalate mentioned above, the green crystals deposited in all old solutions of ferrous oxalate developer may be used. This form of Belitzki's reducer is described in the *Photographic News* for 25th of January, 1884. The green crystals consist of the double oxalate of iron and potash. The reducing solution may then be made up as follows:

Green crystals	¼	ounce
Hypo	1	ounce
Water	5	ounces

Use as before; the chemical action is the same.

We see now the reason why negatives developed with *old* ferrous oxalate are usually *thin.* The ferric oxalate present acts as a reducer.

Belitzki's Durable Reducer.—As an improvement on the method just described, Herr Belitzki gave the following in 1890.

Dissolve in the order given:

Water	200	parts
Ferric-potassic oxalate	10	parts
Sodium sulphite (neutral)	8	parts
Oxalic acid	2½	parts
Of sodium hyposulphite solution (1 to 4)	50	parts

This solution keeps well if filtered and placed in opaque stoppered bottles. It can be used immediately after fixing. It will be noticed that the proportions of this solution are given in "parts." This means *parts by weight.*

These methods of reducing with ferric oxalate are now usually assigned to Belitzki and Eder. But it is practically the same thing as the method for "clearing" negatives described by W. Willis before the Photographic Society of

Great Britain in 1882, and commented on in the *British Journal of Photography* for the 7th of July, 1882. And even before Willis the method had been proposed by Monckhoven.

Lainer's Reducing Bath with Sulphurous Acid.—In the *Photographische Correspondenz* for 1890, A. Lainer recommends the following reducer to be used conjointly with his acid fixing bath:

Hypo	2 ounces
Sodium sulphite	4 ounces
Hydrochloric acid	½ ounce
Water	10 ounces

The negative must be left in this solution until reduction is effected, and the time required for this may be twelve hours. As sulphurous acid is given off, the vessel containing the solution must be provided with an air-tight cover, or it may be covered over and left out of doors.

Valuable Clearing-and-Reducing Agents.—For many years we have recommended that *all* negatives should be passed through the following bath, but they must first have been thoroughly well washed:

Ferrous sulphate	¼ ounce
Hydrochloric acid	1½ drachms
Saturated solution of alum	4 ounces
Water	2 ounces

This clears in a marvellous way the yellow stain caused by development with pyro; and it also slightly reduces. The solution should be kept in motion (by rocking the dish) while upon the negative. Ten minutes in this bath will generally "clear" the negative, which must then be rinsed and washed in running water for half an hour.

Another useful "clearer and reducer" is a saturated solution of alum (say, 10 fluid ounces), to which half an ounce (or less) of strong sulphuric acid has been added. From two to five minutes in this solution will usually be sufficient.

Burton's Reducer.—Harden the gelatine film thoroughly by soaking for an hour in a saturated solution of chrome alum. Wash for ten minutes and dry. Now squeegee on the *back* of the glass a piece of sensitized carbon tissue. When dry expose to light (film facing the light) in a printing frame as usual. Remove, and develop the carbon print by soaking in warm water. The second coating (on the *back* of the negative) will then correct any violent effects in lighting which may be produced by the original negative. This method is best suited for chalky black-and-white negatives, and requires a skilful operator. It is not a reducer in the sense of lessening or changing the substance of the image; but it "reduces" the violent contrasts caused by under-exposure or faulty lighting.

Local Reduction

It is frequently the case that only a small part or parts of a negative require reduction. To obtain local reduction two plans are open to us. We may do it either chemically or mechanically.

1. *Chemical Methods for Local Reduction.*—In this first way the negative should be well soaked in water until the film is quite soft. The surface moisture is then taken off with blotting-paper, and any of the chemical reducing agents which we have described may be applied to the parts requiring reduction by means of a finely pointed camel-hair brush. As an illustration of this method, Professor Vogel relates that a short time ago he "took a view in Torgatten, Norway, of a rocky cave looking out upon the sea. As was expected, the opening of the cave was considerably over-exposed, and was also surrounded by an ugly halo. In order to reduce this portion without affecting the rest, the negative was soaked in water till thoroughly wet, and then the portion *not* to be reduced was dried with strips of blotting-paper. Holding the plate horizontally, a solution of persulphate of iron was applied to the portion to be reduced, while the effect was watched by the aid of the light reflected from a piece of looking-glass held under the negative. The effect was so striking that after a few minutes not only the halo disappeared, but the whole of the over-exposed part of the landscape was reduced to the required density. Nothing remained but to wash the plate in a thorough manner for one hour."

Another method is to paint with some tough varnish all round the part which has to be reduced. Allow the varnish to dry, and then apply the reducing fluid with a brush. Remove the varnish afterwards by warm methylated spirit.

2. *Mechanical Methods for Local Reduction.*—(*a*) In the *British Journal of Photography* for 8th of September, 1882, Mr. W. E. Debenham speaks of "the removal to a certain depth of the gelatine film with the image it bears. This being effected by the rubbing away of part of the negative with a fine cutting powder, such as cuttle-fish bone." The powder may be applied with the tip of the finger. Cigar-ash may be used in like manner.

(*b*) A better method (and, in fact, the best method for local reduction with which we are acquainted) was described by Mr. W. Brooks in the *British Journal* for 1884, p. 633; and 1885, p. 343.

A little strong alcohol (methylated spirit answers well, if of best quality and of specific gravity not higher than .825) is poured into a saucer; the negative is placed on a retouching desk (a printing-frame with the back removed will do) and a sheet of white paper is placed so as to reflect the light through the negative, and so to enable the reduction to be stopped when sufficient. A piece of wash-leather or a fine linen rag is dipped into the alcohol and then rubbed upon the part of the negative which it is desired to reduce. The surface of the gelatine film is gradually rubbed away, and the silver which it contains is seen as a black stain upon the wash-leather. Dip the latter into the spirit every minute or two, and continue rubbing until the over-dense parts have been sufficiently reduced.

It is often marvellous to see how this method will reveal the buried detail in opaque faces, hands, white lace collars, etc., of portraits; or bring to light the tracery of church windows, reduce the halos round them, etc. It is a good plan to tie a piece of cotton-wool inside the wash-leather, so as to make a little pad, which is easy to handle. To rub down fine lines a pointed piece of wood may be covered with wash-leather. White, "snowy" patches in the foregrounds of landscapes are readily "rubbed down." The work is done most easily just after the negative has been dried. With an old negative it is well to soak it in water for an hour, then dry and commence rubbing. Do not be afraid to rub hard, but take care that no grit gets on the rubber or it will cause scratches.

When the reduction seems sufficient (and be careful not to over-do it) rub the film all over with a clean rag and some spirit, which will remove any smears, and take a print to see if the desired result has been obtained.

(*c*) *The Knife.* A method of reduction which requires considerable skill in its use has of late come into great favor among professional retouchers. It consists in the use of a knife-blade ground to a very fine edge and with a rounded point, by which the surface of the gelatine film is carefully scraped away and shaved off in fact, and marvellous alterations effected. By this means ladies' waists are contracted, their hands diminished, etc.; in fact, almost any tricks can be played with the negative. But to do this well requires long practice, combined with manual dexterity. A mezzo-tint scraper is a useful tool where fine lines have to be thinned.

Removal of Stains on Negatives.—The small brown spots or stains seen on most negatives, which have been printed from without being varnished, can generally be removed by the aid of an alcoholic solution of cyanide of potassium of the strength of three grains of the cyanide to each ounce of strong alcohol. The negative should be soaked in this and gently rubbed with cotton-wool. Then soak in alcohol alone, and finally wash well in water and dry.

REDUCTION OF PROOFS ON PAPER.

Reduction of Over-printed Silver Prints on Albumenize Paper.—It is not an easy thing to learn the exact degree of over-printing which is necessary to furnish the "perfect" print, after the slight reduction which it undergoes in the subsequent operations of toning and fixing.

Again, having learned the exact shade or depth required, it is not always the case that the print is removed from the printing-frame at the right moment. With the professional printer, whose whole time is given to the looking after a large number of frames, doubtless the percentage of prints spoiled by over-printing is very small; but with the average amateur it is large. Other objects direct his attention; the power of the light is under-estimated, and then, when the frame is opened, the print is "as black as my hat."

Several attempts have been made to discover processes by which such over-printed prints could be made passable. As a rule these processes result in failures. Not that they do not *reduce* the prints; but that at the same time the tone or color of the prints is altered, and for the worse, while mealiness is frequently produced.

But it is not unfrequently the case that it is desirable to save the print, even if the result be somewhat inferior to what we could desire. In such cases the following methods may be tried:

Reduction of Prints with Hypo.—If the over-printing be only slight, reduction may be effected by leaving the print for an hour or two in a fresh solution of hyposulphite of soda. Given time enough, the hypo will dissolve the finely divided silver of which the image is composed. The hypo bath used for this purpose should be fairly strong (say 6 ounces of hypo to 20 ounces of water), and its temperature should be about 70 deg. Fahr.

2. *England's Method with Cyanide of Potassium.*—In 1881 Mr. William England recommended* a bath "of only four drops of saturated solution of cyanide of potassium to a pint of water" for the reduction of silver prints.

In this extremely weak bath the prints show no signs of change until about an hour has elapsed. They must then be removed, washed well in water, and dried. Cyanide of potassium had been used for a like purpose long before 1881, but not with success. The new point in this method consists in the extremely dilute state in which the solution is employed. Chemically speaking, the action is simply that the cyanide combines with the silver to form a soluble compound.

3. *Dunmore's Method with Mercury Bichloride*, 1890.—Make up the following solution:

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* "Journal of the Photographic Society," New Series, Vol. V., p. 138.

Mercury bichloride	12 grains
Potassium bromide	12 grains
Water	4 ounces

In this immerse the dark prints, and watch them carefully until they are of the right depth, which will be in a few minutes. Mr. Dunmore states that prints which he treated in this way ten years ago have not faded. The solution can be used repeatedly until its strength is exhausted.

4. *With Common Salt.*—After the dark prints have been toned, fixed, and dried, they are placed in fresh hypo solution of the usual strength, to which a little methylated spirit has been added. The following answers well:

Hyposulphite of soda	2 ounces
Methylated spirit	2 ounces
Water	10 ounces

After soaking for ten minutes transfer the prints to a saturated solution of common salt, and after five minutes put them back into the hypo again. With extremely black prints about five drops of a saturated solution of cyanide of potassium may be added to the salt bath.

5. *With Alkaline Ferridcyanide.** — Farmer's reducer, which has met with so much favor for reducing negatives, has been condemned for prints; but by the addition of an alkali it is, according to Mr. Sherman, capable of acting as efficiently upon over-printed silver prints as upon negatives. Make up the following stock solutions:

A.—Ferridcyanide of potassium	1 ounce
Water	1 pint
B.—Carbonate of ammonia	1 pound
Water	5 pints

This is a saturated solution.

C.—Hyposulphite of soda	1 ounce
Water	10 ounces

For use, add to C 1 drachm of B, and enough of A to make it a light lemon color.

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* W. H. Sherman, in "Photo Mosaics," for 1888.

Put the mixture in a white dish and immerse the prints to be reduced (one at a time) in it. Remove them to a bath of salt-water (a handful of salt to a gallon of water) when sufficiently reduced. Then wash well and dry. This method also improves yellow prints and prints which have been made on stale paper.

6. By using the chloride of lime toning bath, or by toning with platinum, over-done prints can frequently be persuaded to assume a respectable appearance. Each of these toning methods, in fact, *requires* a certain amount of over-printing.

Reduction of Bromide Prints.—Bromide prints can be reduced in just the same way as negatives.

Reducing Over-Printed "Blue Prints."—1. Soak the prints in

Potassium carbonate	100 grains
Water	12 ounces

They will gradually be reduced. Then rinse, wash for five minutes, and immerse for a few seconds in

Acetic acid	25 minims
Water	4 ounces

This brightens up the prints. Finally wash for ten minutes and dry. This method was described by Messrs. J. P. and F. C. Beach in 1888.

2. Dip the prints first into a five per cent. solution of ammonia, and then into hydrochloric acid of the same strength. Dilute these solutions if they act too rapidly.

CLASSIFICATION OF REDUCING PROCESSES.*

The various reducers whose action we have now described, may be arranged in six classes:

First.—A change in the *color* of the film or deposit, whereby it is made more transparent to the chemical rays. Example —(*a*) Clearing of stains, etc., from film by action of mixture of hydrochloric acid and alum. (*b*) Bleaching of film by bichloride of mercury.

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* According to Mr. W. E Debenham.

Second.—A direct solution of a portion of the silver embedded in the gelatine film, and constituting the negative. Example.—(*a*) By ozone-bleach, and other hypochlorites. (These have a chemical action also.)

Third.—A chemical change of a portion of the deposit into a compound, which may afterwards be dissolved in a proper solvent. Example.—Most reducing processes belong to this class, as ferric chloride, mercuric chloride, ferricyanide of potassium, etc. These must be followed by the application of hypo to remove the silver salts which are formed.

Fourth.—A solution or loosening of the gelatine film itself. Example.—The action of bleaching-powder and other hypochlorites. This method is not applicable to collodion negatives.

Fifth.—A rubbing or cutting down of the dry gelatine film, as by the use of alcohol applied on wash-leather, etc.

To these may be added:

Sixth.—Any method of working upon the glass *back* of the negative, as Burton's reducer, or by stretching a piece of tissue-paper over the back and then working upon it with lead-pencil or the stump, by which extreme contrasts are reduced.

MAXIMS FOR THE REDUCING OF NEGATIVES.

1. If the negative is varnished, the varnish must be removed before reducing, by means of warm methylated spirit, aided by gentle friction with a pad of cotton-wool.
2. The negative must be thoroughly well washed to free it from hypo before reduction is attempted (except in the special cases noted).
3. Keep the dish in motion while the reducing solution is upon the negative, or the action may be unequal.
4. For negatives which may have been fixed in an *acid* fixing-bath, the "acid ferric oxalate" (durable reducer) of Belitzki should be used.
5. In other cases try *first* the reducing solution of red prussiate of potash followed by hypo (Farmer's reducer).
6. Remove the negative from the reducing solution while

yet a *little* too dense. It will lose slightly in washing and drying.

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CHAPTER XXIX.

INTENSIFYING PROCESSES, AND THEIR CHEMISTRY.

The verb "to intensify" does not belong to the early history of photography. The daguerreotypists (1839–55) do not appear to have endeavored (or at all events were not able) to remedy any deficiency in the depth or density presented by their negatives. As the developing solution left them, so they had to remain. If the photographer was not then satisfied with the picture on his silver plate, his sole remedy was to take another negative.

Whether this is not still the best plan to adopt is an open question—probably it is. But soon after the advent of the calotype process in 1841, a method of increasing the density or opacity of the developed negative was discovered, and this method was found to be still more applicable to the collodion process (1851) which displaced both calotype and daguerreotype. To such a process the name of *intensification* was given.

The idea of intensification is not contained in Snelling's "Dictionary of the Photographic Art," published in New York in 1854. In Sutton's "Dictionary of Photography" (London, 1868), he alludes to the subject only under the head of "development," but in the second edition of this book (1867) we find a very good definition of "Intensifiers":—"This term is used to denote those substances which, when applied to a negative, serve to increase the actinic opacity of the deposit already formed. One class of intensifiers acts by increasing the deposit of silver forming the image. To this class belong a mixture of protosulphate of iron and nitrate of silver, also pyrogallic acid and nitrate of silver. The latter method is most commonly adopted.

"Another class of intensifiers derives its value not from forming any new deposit, but from changing that already formed to a more non-actinic color. To this class belong the alkaline sulphides, which blacken the silver deposit; and Schlippe's salt, which turns the deposit to a very non-actinic scarlet color. Several other substances act after this fashion, but, as a rule, they are inferior to the first class."

Intensification of Calotypes or Talbotypes.—It will be remembered that the calotype negatives (consisting of silver iodide on paper) were developed by means of a solution of gallic acid. One of the best-known text-books on this process, "Thornthwaite's Guide to Photography," 1852, adds (page 84): "Development can be singularly accelerated by adding a few drops of aceto-nitrate of silver, when the image begins to develop itself; and very intense blacks are obtained by this method." That is, a thin image being produced by the developer proper (the gallic acid), this image was able to attract to itself more silver from the mixture of acetic acid and silver nitrate which constituted an *intensifier*, and the image was thus able to build itself up, and to increase in density.

Intensification of Albumen Negatives.—The albumen process of Niepce de St. Victor, 1847, consisted in forming silver iodide upon a glass plate coated with white of egg (albumen). After exposure in the camera, the image was developed by pouring over it a saturated solution of gallic acid. Mr. Malone* writes: "A negative image is the result. At this point previous experimentalists have stopped We have gone further, and find that by pouring upon the surface of the reddish-brown negative image during its development a strong solution of nitrate of silver, a remarkable effect is produced. The brown image deepens in *intensity* until it becomes black."

Of the same albumen process Mayall also wrote (Hunt, 1851): "After development, should the image be still feeble, pour off the gallic acid, rinse the proof with water, and pour on to it equal quantities of aceto-nitrate of silver and gallic acid reduced one-half with water. The image will now quickly develop."

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* One of the best known of the early practical workers in photography." The quotation is from "Hunt's Photography," 1851.

Intensification of Collodion Negatives.—The method of intensification just described was applied but seldom in the case of calotype and albumen negatives, but became quite a constant practice in the development of *collodion* negatives. The great text-book of the worker with collodion was "Hardwich's Manual of Photographic Chemistry," of which nine editions appeared between 1855 and 1883. In the first edition stress is laid on a clear understanding of the word *intensity*, which "relates to the appearance of the finished photograph, independently of the time taken to produce it; *to the degree of opacity of the reduced silver*, and the extent to which it obstructs transmitted light."

The film on a collodion plate consisted of iodide of silver in collodion; but this was exposed wet, and covered with a solution of nitrate of silver. The action of light produced a change in the silver iodide; and development was effected by pouring over the plate either a solution of pyrogallic acid, or one of ferrous sulphate. The result of this was to decompose the nitrate of silver, and the metallic silver was then *deposited upon* the image produced by light.

Thus a collodion plate was developed from *above;* and the picture could often be seen to stand out distinctly in fine relief upon the surface of the collodion.

But the layer of silver nitrate upon the surface of a collodion wet-plate was very thin (for the plates were drained after removal from the nitrate bath, and before exposure), and its silver was soon exhausted. The developed image was consequently too weak and thin. Hardwich (1855) then recommends the following intensification: In development "the pyrogallic acid is to be used alone, until the image has reached its maximum of intensity, which it will usually do in a minute or so, according to the temperature of the developing-room. The plate may then be examined leisurely by placing it in front of, and at some distance from, a sheet of white paper. If it is not sufficiently black, add about 2 drops of silver nitrate solution to each drachm of developer, stir well with a glass rod, and continue the action until the requisite amount of intensity is obtained."

Intensification in this way might really be styled "re-development," or "continued development." It was effected *before* the plate was fixed.

Intensification of Collodion Negatives after Fixing.—In the second edition of Hardwich (1855), he adds to the paragraph quoted above: "When there is any disposition in the plate to *fog* towards the end of the development, it may sometimes be obviated by fixing with cyanide of potassium as soon as the 'development proper' is complete, and then after a careful washing intensifying with pyrogallic acid and nitrate of silver in the usual way."

In the third edition (1856) of this classical book, the subject is put in a very masterly way: "*Mode of Increasing the Intensity of the Negative Image.*—For the sake of clearness, we establish two stages in the development of a collodion negative; first, the *development proper*, or bringing out of an image distinct in all its details by transmitted light; but pale and comparatively translucent; second, *the development by precipitation*, as it has been termed, by which the image is rendered darker and more opaque.

"The strengthening of a feeble image is effected by pouring over the plate a mixture of pyrogallic acid and nitrate of silver. These two substances decompose each other even without the aid of light, and a deposit of silver is formed *which settles down upon the image and adheres to it.* * * * *

"The collodion image is sometimes spoken of as being *within* the substance of the transparent film. This, however, is incorrect; it is really *upon* the surface of the film, and is formed by a *superposition* of metallic particles rather than by a penetration inwards. The mere act of varnishing the plate will often prove this to be the case; the elevated lines of the impression being seen to form an obstruction to the flow of the spirit, and so to produce a series of permanent ridges at various parts of the plate."

This is one of the main points of difference between the *gelatine* and the collodion processes. In the gelatine dry-plate, the silver image is *within* the film, and forms from the surface *downwards.* But silver is *added* to the collodion film during or after development to strengthen the image (which is upon the surface only), and this added silver intensifies or builds up upon the delicate surface-image which has been produced by light.

In the last (ninth) edition of Hardwich, which was published in 1883, we get a masterly summing-up of the whole matter as follows (page 128): "*The Second Stage of the Development.* This consists in strengthening the image first formed, by an additional deposit of silver. Take a sensitive collodion plate, and having impressed an invisible image upon it by a proper exposure in the camera, remove it to the dark-room, and pour over it a solution of pyrogallic acid. When the picture has fully appeared, stop the action by washing the plate with water. An examination of the image at this stage will show that it is perfect in the details, but pale and translucent.

"Now take the plate and treat it with pyrogallic acid to which fresh nitrate of silver has been added; immediately the picture will become much blacker, and will continue to darken even to complete opacity, if the supply of nitrate be kept up. The same result may be obtained after the iodide of silver has been removed from the plate by hyposulphite of soda or cyanide of potassium; and in such a case it is evident that the additional deposit upon the image must be produced from the nitrate of silver, and not from the iodide of silver. Observe also, that this additional deposit *forms only upon the image*, exhibiting no affinity for the unaltered iodide upon the part of the plate corresponding to the shadows of the picture, but attaching itself in preference to those parts already blackened by the developer.

"The second stage of the development, in which a feeble image is strengthened and rendered more opaque, is a process bearing a close resemblance to the growth of a crystal in a saturated liquid by aggregation of fresh particles; and after the picture has reached its full density, a series of elevations may often be seen upon the plate, corresponding to the lines of the image."

The chemistry of intensification with silver is identical with that of development. The silver is reduced to the metallic state, and is attracted by and deposited upon the already existing image. The method is—as we have already pointed out—only *a continuation* of development.

Intensification of Collodion Plates with Mercury.—The curious effect of the compound of mercury and chlorine known as mercuric chloride, or bichloride of mercury ($Hg\ Cl_2$) was noticed very early in the history of photography.

In an important paper "On the Chemical Action of the Rays of the Sun," etc., communicated by Sir John Herschel to the Royal Society* in 1840, he writes: "By far the most remarkable fixing process with which I am acquainted, however, consists in washing over the picture with a weak solution of corrosive sublimate,† and then laying it for a few moments in water. This at once and completely obliterates the picture, reducing it to the state of perfectly white paper, on which the nicest examination (if the process be perfectly executed) can detect no trace, and in which it can be used for any other purpose, as drawing, writing, etc., being completely insensible to light. Nevertheless, the picture, though invisible, is only dormant, and may be instantly revived in all its force by merely brushing it over with a solution of a neutral hyposulphite, after which it remains as insensible as before to the action of light. And thus it may be successively obliterated and revived as often as we please. It hardly requires mention that the property in question furnishes a means of painting in mezzotinto (*i.e.* of commencing on black paper and working in the lights), as also a mode of secret writing, and a variety of similar applications."

This discovery by Herschel contains the foundation of all that was done afterward with mercury bichloride as an intensifying agent. It is true that Herschel hardly recognizes that an *increase* in the intensity of the picture is produced by his method, although the words, "revived *in all its force*," show that he was impressed by the vigor of the results.

It may be thought that this important paper by Herschel was "buried," and inaccessible to most photographers in the medium (Phil. Trans.) in which it was published; but most of its facts were utilized (with due acknowledgment) in Hunt's well-known text-book, "Researches on Light," the first edition of which appeared in 1844. Hunt repeats and extends Herschel's experiments with mercury bichloride.

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* "Philosophical Transactions," Part I. for 1840; p. 1.

† This is the common or trivial name for mercuric chloride.

In the year 1840 Robert Hunt contributed a paper to the "Philosophical Transactions of the Royal Society,"* in which he describes sundry attempts that he had made to obtain daguerreotypes upon *paper*. He says: "If one of the above papers, when removed from the mercurial vapor, be dipped into solution of mercury bichloride, the drawing disappears; but after a few minutes it is seen, as if by magic, unfolding itself, and gradually becoming far more beautiful and whiter than before; delicate lines, before invisible or barely seen, are now distinctly marked, and a rare and singular perfection of detail given to the drawing." Herschel's pictures became, and *remained* invisible after treatment with mercury bichloride because a *white* image was produced upon a *white* surface; but Hunt used a black-surfaced paper, so that the white image was distinctly visible upon the black background.

In the first edition of "Hunt's Text Book of Photography," the preface of which is dated July, 1851 (and which must therefore have been written *prior* to Archer's communication to the *Athenæum*, which we notice further on), he carries the idea of the use of bichloride of mercury as an intensifier a little further. Not that he actually describes its use for this purpose; but he gives notes from which other workers could doubtless get the idea of using the mercury salt for the purpose of intensification. He writes (p. 190): "Dip one of the daguerreotype pictures, formed on the sulphuretted paper† into a solution of corrosive sublimate; the drawing instantly disappears, but, after a few minutes it is seen unfolding itself, and gradually becoming *far more distinct* than it was before, delicate lines, before invisible, or barely seen, are now distinctly marked, and a rare and singular perfection of detail given to the drawing."

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* Vol. for 1840; p. 325.

† The "sulphuretted paper" was paper blackened with sulphide of silver.—W. J. H.

Frederick Scott Archer Publishes a Mercury-Hypo Process of Intensification in 1851.—Archer did three notable pieces of work in photography in the year 1851. First, of course, comes the collodion process itself, which he announced in *The Chemist*, in March, 1851. Next, he showed that pyrogallic acid was superior to gallic acid as a developing agent; and in the last month of the year he described a process of intensification which (slightly altered by the substitution of ammonia for hypo) is the most frequently employed of any at the present day.

In the *Athenæum* for December 20, 1851, p. 1350, Archer writes: "I wish to communicate a peculiar process of *whitening* and blackening the collodion pictures, which may possibly prove interesting.

"The picture being thoroughly washed in plenty of water, after fixing with hyposulphite of soda, is treated in the following manner: Prepare a saturated solution of bichloride of mercury in muriatic* acid. Add one part of this solution to six of water; pour a small quantity of it over the picture at one corner, and allow it to run evenly over the glass. It will be found immediately to deepen the tones of the picture considerably, and the positive image will almost entirely disappear; but presently a peculiar whitening will come on, and in a short time a beautifully delicate white picture will be brought out.† The negative character of the drawing will be almost entirely destroyed, the white positive image alone remaining. This picture, after being well washed and dried, can be varnished and preserved as a positive; but nevertheless, even after this bleaching, it can be changed into a deep-toned negative, many shades darker than it was originally, by immersing it, after a thorough washing, in a weak solution of hyposulphite of soda. In a short time the white picture will entirely disappear, and a black negative image will be the result. It is very singular that the picture can be alternately changed from white positive to black negative many times in succession, and very often with improvement to the picture. By the above process a most perfect white or a deep black negative picture can be obtained, quite distinct from each other."

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* This was the name by which hydrochloric acid was formerly known.—W. J. H.

† Under the name of the "alabastrine process" such pictures became quite the vogue a few years later.—W. J. H.

In the French photographic journal, *La Lumière*, for 24th September, 1853, M. Disderi describes the application of the above process to the intensification of negatives on *paper*, which was accomplished, he says, with complete success.

Hunt wrote to the *Athenæum* (p. 23, for Jan., 1853), claiming that both Herschel and himself had already published a similar process to that described by Archer. The latter, in reply (p. 87), states that he was unaware of Hunt's paper in the Phil. Trans.; and that his process, being upon collodion, was different to Hunt's, which was upon paper.

Maconochie "Deepens" Negatives with Gold.—In the *Photographic Journal* for August, 1853, the following process, devised by Professor Maconochie, of Glasgow, is headed "Method of Deepening Negatives." To 1 ounce of distilled water are added 3 grains each of ammonium chloride and gold chloride. The developed and washed (wet collodion) plate darkens rapidly when this solution is poured over it. In the same periodical for February, 1856, Mr. Titterton recommends the gold solution to be applied to a plate which has already been intensified with mercury, if a *considerable* increase of density be desired.

The chemical change which takes place is, of course, the substitution of gold for silver.

$$\underset{\text{Silver}}{3Ag} \underset{\textit{and}}{+} \underset{\text{Gold Chloride}}{AuCl_3} \underset{\textit{produce}}{=} \underset{\text{Gold}}{Au} \underset{\textit{and}}{+} \underset{\text{Silver Chloride.}}{3AgCl}$$

Halleur Combines Intensification with Fixing in 1853.—In the German text-book of photography written by Dr. Halleur in 1853, and of which a translation was published in England in 1854, we are told (p. 44) that in the calotype process "the picture may be fixed also by washing it with a solution of chloride of mercury (corrosive sublimate), rinsing it subsequently in water and letting it dry. This operation renders the picture perfectly invisible, and leaves, in the case of silver chloride paper, a white, in that of iodide paper a yellowish surface. But the invisible picture may be brought to light at any time by washing with a solution of hyposulphite of soda, rinsing in water, and drying."

The collodion process is not mentioned in this work; it had probably hardly reached Germany at the time the book was written.

Maxwell-Lyte Intensifies Collodion Negatives with Mercury and Potassium Iodide.—In the first volume of the *Journal of the* (London) *Photographic Society*, published in 1853, one of the leading amateurs of the day, Mr. F. Maxwell-Lyte, writes (p. 128): "I first of all whiten the picture by means of the solution of bichloride of mercury in hydrochloric acid, of which, according to Archer's method, I take one part to six of water; and then, after well washing the plate, I pour on a weak solution containing about 2 grains to the ounce of iodide of potassium; by this means a fine yellow picture is produced quite impervious to actinic rays."

The change from white to yellow would, in this case, be produced by the conversion of the *white* salt of mercury (the bichloride) into a yellow salt according to the following equation:

$$\underset{\text{Mercuric Chloride}}{HgCl_2} \underset{\textit{and}}{+} \underset{\text{Potassium Iodide}}{2KI} \underset{\textit{produce}}{=} \underset{\text{Mercuric Iodide}}{HgI_2} \underset{\textit{and}}{+} \underset{\text{Potassium Chloride.}}{2KCl}$$

The yellow compound obstructing especially the rays (blue and violet) which are most effective, the negative is intensified correspondingly.

Donny uses Mercury followed by Sulphuretted Hydrogen, in 1853.—After the appearance in the *Photographic Journal* for 1853 of Maxwell-Lyte's iodide process of intensification (which we have just described), a correspondent wrote (F. Hudson, p. 164), complaining of difficulties caused by the iodide of mercury being soluble in the other solutions employed. This called forth a letter (p. 186) from Professor F. Donny to the following effect: "During last summer I converted into very dark black negatives a good many instantaneous collodion positives, by means of the following process: After development the picture is washed, drained, and immediately whitened according to Archer's method; being carefully washed again with rain-water and drained, but not dried, I cover it with a solution of

Gum arabic—by weight	1 part
Water—by weight	10 parts

"Whilst this gummy covering is still moist, the picture is exposed, in a vertical position, to a strong current of sulphuretted hydrogen, which converts it rapidly into a black negative. The operation is then at an end, and the picture is set up to dry; nothing of the former positive appearance is to be seen on it, even when the glass side is turned towards the eye. In this way black negatives of the utmost darkness are obtained, and will prove much more satisfactory than the yellow ones procured by the iodide process."

What is the chemical change which takes place by this method?

$HgCl_2$ + SH_2 = HgS
Mercuric Chloride *and* Sulphuretted Hydrogen *produce* Mercuric Sulphide
+ $2HCl$
and Hydrochloric Acid.

It is hardly necessary to remark that the offensive smell of sulphuretted hydrogen ("rotten-egg gas") would deter most photographers from even testing this method.

Mercury followed by Ammonia as an Intensifier; used by Hunt for Collodion Negatives in 1853.—The first notice which we have been able to find of the most commonly adopted process of intensification of the present day—mercury, followed by *ammonia*—is contained in the third edition of "Hunt's Manual of Photography." This edition bears the date 1853 on its title-page; but as the preface is dated December, 1852, the discovery must have been made during the latter year.

Writing of collodion negatives, Hunt says (p. 268): "A peculiar whitening process was introduced by Mr. Archer, which is as follows: The picture being thoroughly washed in plenty of water, after fixing with hyposulphite of soda, is treated in the following manner: Prepare a saturated solution of bichloride of mercury in muriatic acid. Add one part of this solution to six of water. Pour a small quantity of it over the picture at one corner, and allow it to run evenly over the glass. It will be found immediately to deepen the tones of the picture considerably, and the positive image will almost disappear; presently, a peculiar whitening will come over it, and in a short time a beautifully delicate white picture will be brought out.

"The negative character of the drawing will be entirely destroyed, the white positive alone remaining. This picture, after being well washed and dried, can be varnished and preserved as a positive; but, nevertheless, even after this bleaching, it can be changed into a deep-toned negative, many shades darker than it was originally, by immersing it, after a thorough washing, in a weak solution of hyposulphite of soda, *or a weak solution of ammonia.* The white picture will vanish, and a black negative will be the result.

"It is very singular that the picture can be alternately changed from a white positive to a black negative many times in succession, and very often with improvement.

"Thus, by the above process, a most perfect white positive, or a deep black negative is produced, quite distinct from each other.

"In the first part of this after-process it will be observed that the effect of this bichloride of mercury solution is to deepen the shades of the picture, and this peculiarity can be made available to strengthen a faint image, by taking the precaution of using the solution weaker, in order that the first change may be completed before the whitening effect comes on. The progress of the change can be stopped at this point by the simple application of water."

The chemical changes produced during this method of intensification are explained further on, when treating of the process as applied to gelatine negatives.

Intensification according to Hardwich.—The nine editions of Hardwich's "Photographic Chemistry" (1855–83), form a sort of guide to photographic progress.

In the first edition (1855), we have two pages on "The Means Employed to Strengthen a Finished Impression which is too feeble to be used as a Negative." It is pointed out that the plan of "pushing," or re-developing, which we have already described as performed with pyro and silver, "cannot be applied with advantage after the picture has been washed and dried." Three plans of intensification are then given:

(1) *Donny's Method*, with mercury bichloride followed by sulphuretted hydrogen or hydrosulphate of ammonia.

(2) *Barreswil and Davanne's Process*,[*] by which the image is converted into iodide of silver, by treatment with iodine, exposed to light, and then re-developed.

(3) *Hunt's Method*, with mercury chloride followed by ammonia.

The second (1855) and third (1856) editions of Hardwich show no change; but the fourth (1857) adds cyanide of potassium as a substance which may be used to blacken the image after the application of mercuric chloride.

The sixth edition (1861) states (p. 170) that "the writer dispenses entirely with the employment of the bichloride of mercury, and acts on the image with a solution of iodine in iodide of potassium until it is converted into iodide of silver, after which the hydrosulphate of ammonia is applied in the usual way."

The ninth and last (1883) edition gives sulphide of ammonium, and cyanide of silver dissolved in cyanide of potassium, as other substances which may be used to blacken the white image produced by the application of mercury bichloride.

Intensifying with Platinum.—Immerse the negative in a solution of platinum tetra-chloride, of the strength of about twenty grains to the ounce. The following change then takes place:

$PtCl_4$	+	$2Ag_2$	=	Pt	+	$4AgCl$
Platinum Chloride	*and*	Silver	*produce*	Platinum	*and*	Silver Chloride.

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[*] This appeared in the *Chimie Photographique*, and was translated in the *Photographic Journal* for August, 1854. The method is strongly recommended by R. J. Fowler in the same *Journal* for May, 1857.

The silver of the original image thus changes place with the platinum.

The Platinotype Company sell a one-solution intensifier which Captain Abney states "is composed of mercuric chloride and a salt of platinum." It acts by changing the image to an orange-brown color.

Schlippe's Salt as an Intensifier (*Carey Lea*).—In the year 1865, Mr. Carey Lea, the famous American photo-chemist, announced[*] a method of intensification by the use of Schlippe's salt (sodium sulphantimoniate), which has since proved of service, especially where a considerable increase in the opacity of the negative is desired. As recommended by Lea for collodion negatives, the method consisted in converting the silver of the image into silver iodide, which was then reddened by the Schlippe's salt. For gelatine negatives it is better to convert the silver into silver chloride by soaking the negative in a bath of ferric chloride (say twenty grains to the ounce):

Fe_2Cl_6	+	Ag_2	=	$2AgCl$	+	$2FeCl_2$
Ferric Chloride	*and*	Silver	*produce*	Silver Chloride	*and*	Ferrous Chloride.

Now wash the negative thoroughly, and immerse it in a bath of Schlippe's salt (strength, say a saturated solution, diluted with an equal volume of water) when the image will be converted into silver sulphantimoniate, which is of a scarlet hue.

$3AgCl$	+	Na_3SbS_4	=	Ag_3SbS_4	+	$3NaCl$
Silver Chloride	*and*	Schlippe's Salt	*produce*	Silver Sulphantimoniate	*and*	Sodium Chloride.

The scarlet substance is very opaque, and the intensification is correspondingly considerable. The process is, in fact, better suited for reproduction of line engravings, etc., than for landscape negatives.

The negative must finally be washed and dried.

Intensifying Collodion Negatives with Quinol.—In 1888 Captain Hubl recommended[†] the use of quinol (hydroquinone) for intensifying collodion negatives, as follows:

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[*] *British Journal of Photography*, Vol. XII., pp. 55, 288.

[†] See paper by Dr. Eder in *Photographic News* for January 3, 1890.

Solution A.

Hydroquinone	10 parts
Citric acid	6 parts
Water	1000 parts

Solution B.

Nitrate of silver	1 part
Water	30 parts

For use, mix 3 ounces of a A with 1 of B.

Intensification of Gelatine Negatives: I.—Intensifiers Containing Mercury.

The collodion process was displaced—for general work—by gelatine in the years 1879 to 1881.

Gelatine dry-plates consist of an emulsion of silver bromide in gelatine, spread upon glass or celluloid. By exposure to light, the silver bromide suffers a chemical change, though the precise nature of that change has not yet been ascertained with certainty. The only point in dispute, however, is as to whether the non-metallic element bromine is separated altogether, or only in part (and if in part, how much?) from the metallic silver. For simplicity let us here suppose that the effect of light is to form a picture in metallic silver upon the surface of the gelatine emulsion. This picture is so weak that it is invisible; but when the developer (usually an alkaline solution of pyrogallic acid) is poured over the plate, it enables the reduced silver to attack and decompose the silver bromide *lying beneath* it; and thus the image *grows downwards*, and becomes visible at last when the *back* of the plate is examined. This is just the opposite of the action of development on a collodion plate. On the latter the image is built up from without, and upwards; on the gelatine plate from within, and the image grows downwards.

Negatives on Gelatine Plates Frequently Require Intensifying.—After a gelatine dry-plate has been exposed in the camera, and then developed, fixed, and washed to the best of the manipulator's ability, it is frequently found to give a very unsatisfactory print. In this case intensification *may* effect an improvement. It is a good plan always to take a print from any negative *before* intensifying it. Many negatives print better than they look; and in any case the print affords a means of subsequently estimating what improvement—if any—has been effected.

There are three principal causes for which intensification is supposed to offer a remedy.

1. Under-development.
2. Under-exposure.
3. Over-exposure.

We believe, however, that it is only in the last case, viz: thinness from over-exposure—that the intensifying process offers any real advantage. In *any* case the *best* remedy is—to take another negative. But where, from moderate over-exposure, a negative shows a delicate, thin image, full of detail, it may, by intensification, be made to yield a passable print. This is one reason why all the text-books agree in recommending workers generally to err—if in doubt—on the side of *over*-exposure.

INTENSIFICATION OF GELATINE NEGATIVES WITH MERCURY BICHLORIDE; FOLLOWED BY AMMONIA OR SOME OTHER DARKENING AGENT.

1. *Intensification by Mercury Bichloride Alone.*—Make up the following solution:

Mercury bichloride (corrosive sublimate)........	¼ ounce
Ammonium chloride (sal ammoniac)............	¼ ounce
Hydrochloric acid..............................	10 minims
Distilled water................................	10 ounces

Dissolve the sal ammoniac in the acid water; then powder the corrosive sublimate in a mortar, and add it to the solution. Shake well at intervals, and allow to stand for a few hours; then filter. The addition of the sal ammoniac enables the water to more readily dissolve the mercurial salt. The bottle should be labelled *poison.*

The negative to be intensified should be thoroughly washed after being developed; it should then be soaked for half an hour in an alum bath; and then washed again in running water for one hour. It must then be allowed to dry.

It is a good plan to keep one dish—a glass one is to be preferred—specially for the work of intensification, as the solution employed will injuriously affect both negatives and prints which do not require its aid.

Soak the dried negative in water for ten minutes, and then place it in the mercury solution. Rock the dish gently. The image steadily whitens, until at last it becomes clearly visible as a beautiful positive. The chemical change is expressed by the following equation:

Ag_2	+	$2HgCl_2$	=	$2AgCl$	+	Hg_2Cl_2
Silver	*and*	Mercuric Chloride	*produce*	Silver Chloride	*and*	Mercurous Chloride.

Thus the white substance of which the image is now composed is a mixture of silver chloride and mercurous chloride (commonly called calomel).

The image, after this process, is slightly stronger and denser than before. But, being composed of white and somewhat translucent matter, the print which it now yields is only a slight advance in the above respects over that given by the original unintensified plate.

By acting upon the whitened image with one or other of several re-agents, it is possible to *change its color* to one which shall better obstruct the rays of light. The intensification will then be much more marked.

Blackening with Ammonia.—The plate which has been whitened by the mercury bichloride must receive a very thorough washing if the next process which it has to undergo is to be productive of permanent results. Rinse it thoroughly in two or three changes of water, and then wash it in running water for at least half an hour. The mercurial salt is much more soluble in water to which a little ammonium chloride has been added, than in water alone. Therefore soak the negative for ten minutes in water, 5 ounces, ammonium chloride, $\frac{1}{4}$ ounce.

While this is being done, prepare the following solution:

Ammonia (strong).......	2 drachms
Water..	10 ounces

Place this alkaline solution in a clean dish, and immerse the washed and whitened negative therein. Its color quickly changes—first to brown and then to black. What is the cause of this?

$$\underset{\text{Calomel}}{\mathrm{Hg_2Cl_2}} \underset{\textit{and}}{+} \underset{\text{Ammonia}}{2\mathrm{NH_3}} \underset{\textit{produce}}{=} \underset{\substack{\text{Mercurous-ammonium}\\ \text{Chloride.}}}{2\mathrm{NH_3HgCl}}$$

The silver chloride is dissolved by the ammonia, and is washed away.

The image is now weaker in point of quantity of material, than it was before the application of the ammonia; for the silver chloride has been removed. But the change of color has made it more opaque. If the negative be now washed for five minutes, and then dried, it will (supposing it to have been thin and over-exposed to begin with) probably yield a much better print than before this process of intensification was carried out.

If twice the quantity of ammonia named above be used (4 drachms instead of 2), a somewhat blacker negative will be obtained.

If the application of ammonia produces, or is followed by spots and stains, it is a sign that the negative has not been thoroughly freed from hypo by washing.

Blackening by Sodium Sulphite.—Instead of using ammonia, the whitened negative may be changed in color by immersion in a saturated solution of sulphite of soda, to which half its bulk of water, and two grains per ounce of citric acid, have been added.

Crush two ounces of clear crystals of sodium sulphite in a mortar and add eight ounces of water. This ought to just dissolve the solid sulphite. Then add four ounces more of water, and shake well. This solution should be used soon after it has been prepared. The chemical action is now as follows:

$$\underset{\text{Calomel}}{\mathrm{Hg_2Cl_2}} \underset{\textit{and}}{+} \underset{\substack{\text{Sodium}\\ \text{Sulphite}}}{\mathrm{Na_2SO_3}} \underset{\textit{and}}{+} \underset{\text{Water}}{\mathrm{H_2O}} \underset{\textit{produce}}{=} \underset{\text{Mercury}}{2\mathrm{Hg}} \underset{\textit{and}}{+}$$

$$\underset{\substack{\text{Sodium}\\ \text{Sulphate}}}{\mathrm{Na_2SO_4}} \underset{\textit{and}}{+} \underset{\substack{\text{Hydrochloric}\\ \text{Acid.}}}{2\mathrm{HCl}}$$

So that an image in black reduced mercury is obtained. Our own experience with this intensifier is that it imparts *less* density than ammonia. It is therefore a good intensifier for negatives that only require a slight strengthening.

Blackening by Ammonium Sulphide.—When a very considerable increase of density is required, the whitened negative may be soaked in the following solution :

Ammonium sulphide	1 part
Water	20 parts

The ammonium sulphide is a yellow liquid possessing a very disagreeable smell. Its effect is to convert *both* the chlorides of which the whitened image is composed into their corresponding sulphides ; and these are very black and opaque. Take first the action upon the mercurous chloride :

Hg_2Cl_2	+	$(NH_4)_2S$	=	Hg_2S	+	$2NH_4Cl$
Calomel	*and*	Ammonium Sulphide	*produce*	Mercurous Sulphide	*and*	Ammonium Chloride.

A similar change is produced with the silver chloride :

$2AgCl$	+	$(NH_4)_2S$	=	Ag_2S	+	$2NH_4Cl$
Silver Chloride	*and*	Ammonium Sulphide	*produce*	Silver Sulphide	*and*	Ammonium Chloride.

This powerful intensifier is apt, however, to block up and destroy the half-tones. It is well suited, however, for copies of printed matter, etc., in which a dense black-and-white negative is desired.

Blackening by Potassio-Ferrous Oxalate.—To eight ounces of a cold saturated solution of potash oxalate, add two ounces of a cold saturated solution of ferrous sulphate. This is the ordinary "ferrous oxalate" developer. Its use in intensification was first proposed by Messrs. C. I. Burton and A. P. Laurie. (See *British Journal of Photography* for 1881, pp. 287, 294.)

When the whitened negative is soaked in the above mixture, the haloid salts are quickly reduced to the metallic form, and we get the original silver image back again, plus an image in mercury.

The effect upon the silver haloid is as follows:

$$\underset{\text{Silver Chloride}}{2AgCl} \underset{\textit{and}}{+} \underset{\text{Ferrous Oxalate}}{2FeC_2O_4} \underset{\textit{and}}{+} \underset{\text{Potash Oxalate}}{K_2C_2O_4} \underset{\textit{produce}}{=} \underset{\text{Silver}}{Ag_2} \underset{\textit{and}}{+} \underset{\text{Ferric Oxalate}}{Fe_2(C_2O_4)_3} \underset{\textit{and}}{+} \underset{\text{Potassium Chloride.}}{2KCl}$$

Upon the mercurous chloride (calomel) a similar effect is produced:

$$\underset{\text{Calomel}}{Hg_2Cl_2} \underset{\textit{and}}{+} \underset{\text{Ferrous Oxalate}}{2FeC_2O_4} \underset{\textit{and}}{+} \underset{\text{Potash Oxalate}}{K_2C_2O_4} \underset{\textit{produce}}{=} \underset{\text{Mercury}}{2Hg} \underset{\textit{and}}{+} \underset{\text{Ferric Oxalate}}{Fe_2(C_2O_4)_3} \underset{\textit{and}}{+} \underset{\text{Potassium Chloride.}}{2KCl}$$

The mixture of the two metals (silver and mercury) in a finely-divided state, gives a dark and opaque image. Additional intensity can be imparted by whitening the negative a second time with mercury bichloride, and then repeating the operation with ferrous oxalate as before.

Blackening with Potassio-Silver Cyanide.—Dissolve 120 grains of silver nitrate in 10 ounces of distilled water; and add to it, drop by drop, a strong solution of potassium cyanide, until the white precipitate at first formed is *just* dissolved (stir with a glass rod). The solution ought then to look opalescent, or as if a drop of milk had been added to the water. Soak in it the negative which has been bleached with mercury bichloride (as already described) until it is quite black, as seen from the back. Then wash for an hour, and dry. This method gives a considerable intensification, with very little blocking-up of detail. It is one which we have practised with much success.

Professor Meldola believes that the blackening is due to the following chemical reaction:

$$\underset{\text{Calomel}}{Hg_2Cl_2} \underset{\textit{and}}{+} \underset{\text{Potassio Silver Cyanide}}{2AgK(CN)_2} \underset{\textit{produce}}{=} \underset{\text{Silver}}{Ag_2} \underset{\textit{and}}{+} \underset{\text{Mercuric Cyanide}}{2Hg(CN)_2} \underset{\textit{and}}{+} \underset{\text{Potassium Chloride.}}{2KCl}$$

The blackened image is therefore composed of metallic silver and mercuric cyanide.

This method is due to the late Dr. Van Monckhoven.

Blackening with Hydroquinone.—In 1889 Dr. Mallman, in Germany, and A. R. Dresser, in England, recommended the ordinary developing solution of hydroquinone, as made up with sulphite of soda, to blacken and intensify negatives which had been treated with mercury bichloride. The following solution answers well:

Hydroquinone	20 grains
Sulphite of soda	80 grains
Distilled water	5 ounces

This gives a fine bluish-black color to the negatives.

Intensifying Gelatine Negatives with Mercuric Iodide plus Hypo (Edwards' Intensifier).—In the *British Journal Almanac* for 1880 (p. 56), the well-known plate-maker, Mr. B. J. Edwards, published a method of intensification which has been much used since.

Its latest form is as follows:

Dissolve 60 grains of mercury bichloride in 8 ounces of water. Add to this enough potassium iodide to *nearly* redissolve the red precipitate which is at first formed (about 150 grains will be required). Lastly, add 120 grains of hyposulphite of soda in crystals, and shake well. This should give a clear solution:

$HgCl_2$ + $2KI$ = HgI_2
Mercury Bichloride *and* Potassium Iodide *produce* Mercuric Iodide
+ $2KCl$
and Potassium Chloride.

The negative to be intensified need be only slightly rinsed or washed before transfer to the above solution. It will there quickly gain in printing density.

Lastly, place the intensified negative in a weak fixing-bath (2 ounces hypo to 20 of water), for a quarter of a minute (not more), and then wash well, and dry.

Intensification with Mercuric Bromide followed by Ferrous Oxalate.—Messrs. C. I. Burton and A. P. Laurie described in 1881[*] how to intensify gelatine negatives as follows:

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[*] *British Journal of Photography*, pp. 287, 294.

SOLUTION A.

Mercuric bromide	1 part
Water	250 parts

This is a saturated solution.

SOLUTION B.

Ferrous sulphate (sat. sol.)	1 part
Potash oxalate "	2 parts

Pour the sulphate into the oxalate, and not *vice versa.* The mixture is the ordinary ferrous oxalate developer.

Bleach the negative in A; then wash it, and expose it to sunlight for two or three minutes.

Then apply the developer (B), just as if developing a negative. The image blackens, and gains considerably in density. If still greater density be required, the whole process may be repeated. The plate must be left ten or twenty minutes in the developer in order to thoroughly blacken it. It must then be washed and dried.

The chemistry of this method will be similar to that where mercuric chloride is used, followed by ferrous oxalate.

Gelatine Negatives Intensified by Mercuric Iodide, followed by Schlippe's Salt.—The following method was given in an editorial article in the *Photographic News* for 15th July, 1887:

Make a solution of mercuric iodide by adding a strong (one in five) solution of potassium iodide to a saturated solution of mercury bichloride. About 3¼ ounces of the former to 10 ounces of the latter will be right. The red precipitate which forms should just re-dissolve. For use, add 3 ounces of water to each ounce of the above mixture:

$$\underset{\text{Mercury Bichloride}}{HgCl_2} \underset{\textit{and}}{+} \underset{\text{Potassium Iodide}}{2KI} \underset{\textit{produce}}{=} \underset{\text{Mercuric Iodide}}{HgI_2} \underset{\textit{and}}{+} \underset{\text{Potassium Chloride.}}{2KCl}$$

Soak the plate to be intensified in this solution until it is nearly (but not quite) dense enough. Then wash well for one hour.

Make a solution of Schlippe's Salt (properly called sulphantimoniate of soda) in water of the strength of five grains per ounce. Soak the washed negative in this until the desired density has been obtained; then wash well and dry.

INTENSIFICATION OF GELATINE NEGATIVES. II.—INTENSIFYING WITHOUT MERCURY.

Wellington's Silver Intensifier for Gelatine Negatives.—In the "Photo. Almanac" for 1889 (p. 575), Mr. J. B. B. Wellington writes: "Silver intensification as used for wet (collodion) plates, namely, with nitrate of silver and pyro, is out of the question for the ordinary work of the photographer of the present day, as the hypo has to be thoroughly eliminated from the gelatine film by long-continued washing, and even after this has been done the nitrate of silver has often a persistent habit of staining the film red, and which occurs even in collodion plates.

"I can now carry on intensification without the silver being thrown out of solution, producing a negative of any intensity from the merest ghost of an image, and resembling in character any ordinarily developed negative:

Silver nitrate	100 grains
Distilled water	2 ounces

"Add to this 240 grains of sulphocyanide of ammonium; a precipitate is formed which is again dissolved. On diluting this to ten ounces with water another precipitate is thrown out. Now dissolve this precipitate by adding hyposulphite of soda to the solution. This constitutes the stock solution.

"To intensify take—

Stock solution	1 ounce

"And add—

Pyro	3 grains
Sulphite of soda	12 grains
Ammonia	6 minims
Ammonium bromide	2 grains

"From five to ten minutes will produce a dense negative from a very thin one without staining in the slightest degree.

More ammonia may be added from time to time if not sufficiently energetic. For wet-plates, collodio-bromide, and gelatine, it cannot be surpassed at present."

Intensifying with Uranium (*Selle*).—In the *Bulletin Belge de la Photographie*, for 1865,* M. Hermann Selle showed how to intensify collodion negatives with a mixture of sulphate of uranium and cyanide of potassium and iron; and in 1866 Duncan substituted the nitrate of uranium for the sulphate. Lastly, in his classical book on "Modern Dry-Plates" (1881), Eder showed how useful the method was for gelatine negatives.

Make up the following solution:

Uranium nitrate	20 grains
Potassium ferridcyanide	25 grains
Distilled water	7 ounces

This solution should be perfectly clear. The negative must be soaked in it until it is of a brownish-red color; and then *well* washed.

The uranium and potassium salts combine to form uranium ferricyanide, and this last-named substance combines with the silver (of the image) to produce ferrocyanides of silver and uranium. The uranium ferrocyanide being naturally of a dark-brown color, it is not necessary to use any blackening agent such as is needed in intensifying with lead. Otherwise, the chemical changes which take place are similar, and may be expressed by similar equations.

Intensifying with Lead (*Eder and Toth*).—In the year 1876, two Austrian investigators—Professor J. M. Eder and Captain V. Toth—published† a method of intensifying collodion negatives with lead; the method is also applicable to gelatine negatives.

In the first place it is necessary to prepare ferricyanide of lead, by mixing together the following substances:

Nitrate of lead	4 parts
Red prussiate of potash	6 parts
Distilled water	100 parts

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* Translated in *Photographic News*, 1865, pp. 366, 498; and 1866, pp. 169. 202.

† *Photographic News*, pp. 100, 573, 579, 593, 608.

A chemical change takes place, resulting in the formation of ferricyanide of lead:

$3Pb(NO_3)_2$	+	$K_6Fe_2(CN)_{12}$	=	$Pb_3Fe_2(CN)_{12}$	+	$6KNO_3$
Lead Nitrate	*and*	Red Prussiate of Potash	*produce*	Lead Ferricyanide	*and*	Potassium Nitrate.

Filter the mixture and immerse in it the negative to be intensified. The time required to produce the necessary density is much longer if the negative has been previously dried; it may then take hours. In this case the silver (of the image) combines with the lead ferricyanide to form the ferrocyanides of lead and of silver.

$2Ag_2$	+	$2Pb_3Fe_2(CN)_{12}$	=	$Ag_4Fe(CN)_6$	+	$3Pb_2Fe(CN)_6$
Silver	*and*	Lead Ferricyanide	*produce*	Silver Ferrocyanide	*and*	Lead Ferrocyanide.

These ferrocyanides are white. To blacken them (thereby increasing their opacity) the plate must be *well washed*, and then immersed in ammonium sulphide diluted with five times its volume of water. The white ferrocyanides are thereby converted into the dark *sulphides* of lead and of silver.

This method gives three times greater density than that obtained by the use of mercury and ammonia. It is seldom used at the present day except for "line" work.

Intensification by Permanganate of Potash.—Dissolve quarter of an ounce of the permanganate of potash in eight ounces of water. When any negative which has been developed, fixed, and washed in the ordinary way is immersed in this solution its color is changed to brown. In some cases this treatment alone will give sufficient density, and the negative need then be only washed and dried.

If more density be required, wash the negative, and place it in the ordinary ferrous oxalate developer, when the color will change to black:

$K_2Mn_2O_8$	+	$4Ag_2$	=	$4Ag_2O$	+	Mn_2O_3	+	K_2O
Permanganate of Potash	*and*	Silver	*produce*	Silver Oxide	*and*	Oxide of Manganese	*and*	Potassium Oxide.

The first or brown image consists of a mixture of silver oxide and manganese oxide.

The ferrous oxalate developer reduces the silver oxide to black metallic silver, which is more opaque than the silver oxide.

This permanganate intensifier was used for collodion wet-plates as long ago as 1868, by Mr. Wharton Simpson. In 1890 it was recommended by M. A. Gendrand, in *Le Progrés Photographique*, for gelatine plates. It is better suited for reproductions of engravings, etc., than for ordinary negatives, as its effect is to give very strong contrasts.

Intensifying with Aniline Dyes.—In 1890, Dr. R. E. Liesegang recommended* the varnished negative to be coated with collodion or varnish in which a little of any red or green aniline dye had been dissolved. Such colors, it is well known, are bleached by exposure to light. The *back* or glass side of the negative is then exposed to sunlight, which acts *through* the film upon the dye, decolorizing the latter in proportion to the opacity of the different parts of the image.

The negative is then printed from in the usual way; but the intensifying operations will have to be repeated if many prints are made.

Intensification by the Powder Process.—By this method no chemical change is produced in the image; with which, indeed, the materials employed do not—or need not—come in contact. The back or glass side of the negative is coated with the following mixture:

Albumen	70 minims
Ammonium bichromate (sat. sol.)	150 minims
Honey	90 grains
Water	10 ounces

This mixture is not sensitive while wet; but after drying (in a hot oven) it is much more sensitive than ordinary sensitized paper.

The coated negative is then exposed (the *film* side being towards the sky) for about half a minute to diffused sunlight.

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* In the *Photographisches Archiv.*

Both the exposure and the subsequent printing are best done at the bottom of a deep box just fitting the negative, and placed so that only parallel rays can fall upon the negative.

After exposure, the coated side of the negative is dusted over (in the dark-room) with powdered black-lead applied by means of a brush. This adheres to the coating in exact proportion to the action of the light upon the said coating. Thus a *second* negative is produced behind the first or original negative; and the prints given by the *double* negative are, of course, more "intense" than those from the original film.

By regulating the length of the exposure to sunlight, either the whole, or only the high-lights of the original negative can be intensified.

The powder process was the invention of, or rather was perfected by J. Obernetter, of Munich, in 1874.*

Local Intensification.—It is often desirable to intensify a negative *in part only.* It is then best to soak the negative (if it has been dried) in water for half an hour. Remove the negative and blot off the surface water with a clean towel. Then paint the intensifier by the aid of a small soft brush upon the parts which it is desired to intensify. Wash the negative and complete the operation as usual.

Another plan is to paint with machine oil upon those parts of the negative which do *not* need intensifying; and then to proceed as usual. But there is some difficulty, after the intensification is completed, in removing the oil. It may be cleaned off, however, by ether, or by a little weak soda.

In the "Photo. Almanac" for 1889 (p. 402), G. W. Valentine recommends a mixture of Judson's yellow or orange dyes with half an ounce of gum senegal, applied thinly by means of a camel-hair brush, moistened with the tongue, to those parts of the negative which require intensification.

MAXIMS FOR INTENSIFICATION.

1. In most intensifying processes the negatives must be thoroughly *fixed* and thoroughly *washed* before intensification is

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* *Photographic News* for 1874, pp. 147, 214, 344.

attempted. Sometimes intensification may *precede* fixing; and in one intensifying process (Edwards') the removal of the hypo is of no importance. In all other cases any default in fixing or in washing will result either in immediate failure, or in the appearance of spots or stains upon the film after a short time.

2. The intensifying solutions must be kept in constant *motion* (by rocking the dish) while upon the negative. If this is not done, it is probable that they will act *unequally* upon the image.

3. If a negative shows the least sign of *fog*, it is better to slightly *reduce* it (see chapter on "Reducers") before attempting intensification. If it is *much* fogged, it is useless to attempt intensification at all. Really successful intensification is only possible with negatives which, though thin, are quite clear in the shadows and full of detail.

4. Remember that intensification is only a make-shift. It will generally be found better, easier, and probably cheaper to take another negative (when possible) rather than to intensify a defective one.

5. In choosing a method of intensification, remember that it must suit the negative. Some negatives require but a little, others a great deal, of intensification. Choose your process accordingly.

6. Remember that all intensifiers have their good and their bad points. Silver intensifiers alone do not discolor the negative; but silver nitrate stains the fingers.

Mercurial salts, followed by baths of potassium cyanide or iodide and silver nitrate, etc., give permanent results; but they involve the use of very poisonous substances.

Mercury, followed by ammonia, is the simplest and most used method; but great care must be taken or the results are not permanent.

7. Any stain upon the surface—such as the iridescent stains commonly seen on negatives which have been printed from while unvarnished—will give red spots when intensification is attempted. Such stains may often be removed by gentle friction with a very dilute solution (5 grains to the ounce) of cyanide of potassium, followed by a good washing.

8. If the negative to be intensified has been varnished, the varnish must be removed by soaking the negative in warm methylated spirit. It should then be washed in water and its surface rubbed with a pad of cotton-wool.

Or if collodion has been used instead of varnish to protect the gelatine film, this substance can be removed by soaking the negative in a mixture of alcohol two parts, with ether one part.

9. The various methods for intensification may be arranged in three classes:

(*a*) The piling up of more silver upon the original silver image.

(*b*) The *addition* of some other metal to the silver.

(*c*) The *substitution* of some other metal, as gold or platinum, for the silver.

10. Mercury bichloride is only slightly soluble in water, but much more soluble in water containing ammonium chloride. A speedy way of removing the bichloride is therefore to soak the negative (after rinsing well under the tap) for ten minutes in

Ammonium chloride	1 ounce
Water	10 ounces

Then rinse and wash in running water for twenty minutes.

11. Remember that if the values or gradations of the negative are to be preserved, the intensifying solutions must each be allowed time to produce their full effect; that is, they must act right through the film at every point. By arresting the intensification at an earlier stage the contrasts must be decreased, because the solutions will have penetrated completely through the detail in the shadows, while in the high-lights their work may be less than half done.

CHAPTER XXX.

THE TONING OF PHOTOGRAPHS CONSIDERED CHEMICALLY, HISTORICALLY, AND GENERALLY.

Fizeau Discovers How to Tone Daguerreotypes.

What Is "Toning"?—The term "toning" is used in photography in the sense of "coloring." In fact, the early writers on photography actually used the word "coloring," and not "toning," for the process which we are about to describe.

When an ordinary photograph on paper is taken out of the printing-frame, its color may be pleasant or unpleasant to the eye. With the greater part of the ready-sensitized papers now sold the color is distinctly unpleasant, being a red of uncertain tint. With freshly sensitized paper the color approximates more to violet. But all such prints, if fixed at once without toning, assume a brick-red hue which is inartistic and displeasing to the eye.

To change this red color to brown or black is the object of the photographic process known as "toning." It is effected, for the most part, by depositing finely divided gold upon the silver which forms the picture.

Faraday has shown* that gold in an extremely fine state of division may be of many colors, from ruby to blue. It is the blue form of gold which we desire to deposit upon the red silver of the print in order to "tone" it. The combined effect of the red and the blue is to give the blackish tints which we desire.

The Toning of Daguerreotypes.—The first successful photographic process was that which bears the honored name of Daguerre, and which he published in 1839. The image was formed (in the camera) upon a silver plate covered with iodide of silver, and it was developed by the vapor of mercury. The early daguerreotypes were very weak, indistinct, and unstable productions; and the toning or gilding of them by means of a solution of chloride of gold, as discovered by the French investigator, M. Hippolyte Louis Fizeau, in 1841,* was a great improvement.

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* "Some Observations on Divided Gold:" *Proceedings Royal Institution*, Volume II., for 1854-58; pp. 308-312.

"On the Relations of Gold to Light:" *Proceedings Royal Institution*, pp. 444-46.

"Experimental Relations of Gold (and other metals) to Light" (Bakerian Lecture): *Philosophical Transactions* for 1857, pp. 145-162; also in *Philosophical Magazine* for 1857, pp. 401-512.

After development, the silver plate had its picture "fixed" by immersion in a solution of hyposulphite of soda. The following description of its subsequent treatment is extracted from M. Fizeau's memoir:

"Since the publication of the photogenic processes every one, and M. Daguerre among the first, acknowledged that something yet remained to be done to give these marvellous images that degree of perfection which it is now possible to obtain: I mean the fixing of the impressions and the giving to the light parts of the image more intensity.

"The process which I now submit to the Academy appears to me to resolve in a great measure this double problem; it consists in subjecting the plate to the action of a salt of gold prepared in the following manner:

"Dissolve 1 gramme of chloride of gold in 1 pint of pure water, and 3 grammes of hyposulphite of soda in another pint of water; then pour the solution of gold into that of soda, little by little, and shaking it all the while. The mixture, which is at first of a slightly yellow color, soon becomes perfectly limpid. It would then appear to contain a double hyposulphite of soda and of gold, with the addition of marine salt, which appears to perform no active part in the operation.

"In order that this salt-of-gold process may produce its effect upon the silver coating of the plate, it is important that the latter should be perfectly free from foreign matter, and especially from all greasy particles; it is therefore necessary that it should have been previously washed with great care, which may be dispensed with when you only wish to have recourse to the ordinary wash.

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* "Sur un moyen de fixer les images photographiques": Paris. *Comptes Rendus*, Volume XI., pp. 237-8.

"The following method is the one most generally attended with success: While the plate is yet covered with the coating of iodine, but exempt from all dust and grease, both on the two surfaces and at the edges, pour a few drops of alcohol upon the iodized surface.

"When the alcohol has wetted the whole surface, immerse the plate first in the filtered water, and afterward in the hyposulphite solution. This last must be renewed for each plate, and should contain about 1 part of salt of gold to 15 of water; the remaining part of this washing process is performed in the ordinary way, only care should be taken that the water used should be as much as possible free from dust.

"The alcohol is used simply to cause the water to adhere perfectly to the whole of the surface of the plate, and to hinder it from running off to the sides on each immersion, which would infallibly cause spots.

"When a plate has been washed with these precautions, even if the image was very old, the application of the salt of gold would be the most simple possible. You have only to place the plate upon the wire frame, which is to be found in each apparatus; to pour upon it a coating of the salt of gold, sufficient to cover it entirely, and to heat it underneath with a strong flame. The impression will be found to become distinct, and to assume, in a minute or two, a fine vigorous tone and color. When the effect is produced, the liquid must be poured off and the plate washed and dried.

"In the operation which we have just described, the following phenomena have taken place: Silver has been dissolved, and gold has been precipitated upon the silver, and also upon the mercury, but with very different results. The silver which, by its polish, forms the dark part of the picture, is in some degree browned by the thin coating of gold which covers it, whence results an increased intensity in the black parts; the mercury, on the contrary, which, under the form of infinitely small globules, forms the whites, increases in strength and brilliancy by its amalgamation with the gold, whence result a greater degree of fixity and a remarkable augmentation in the light parts of the image."

Before Fizeau announced this method of gilding or toning, we are told that "the daguerreotype would not resist the slightest touch; a finger passed over it destroyed the whole picture; moreover, it did not long remain intact—a short time sufficed to deprive it of its sharpness."

This paper of Fizeau's was the origin of our system of toning, and, as such, marks an epoch. We note:

1. That it introduces the use of the chloride of gold into photographic processes.
2. The gold chloride was not used alone, but combined with hyposulphite of soda.
3. Toning *followed* fixing.
4. The deposition of the gold upon the image was produced by the agency of *heat*.
5. The permanency and the color of the image were both improved. Gold is a far less oxidizable metal than silver; so that it stands exposure to the air without material alteration, while silver rapidly tarnishes. Its color, too, is superior to that of the silver alone.

The practice of the daguerreotype process has ceased. It ended in England about 1855, and in the United States about 1863. But it was the first practical and commercial process of photography, and it is interesting to trace its influence upon the processes which have superseded it.

History of Toning Processes.

Hardwich upon Toning.—In March, 1855, T. F. Hardwich published the first edition of a book which became so well known among English workers that it was dubbed the "Photographer's Bible." The author was an excellent chemist, and he did much in those early days to put the scientific side of photography upon a sound footing. His book has since passed through nine editions, having been revised by Messrs. Dawson, Hadow and Traill Taylor, the date of the latest edition being 1883; and it is still a sound and useful work. The long period of time (nearly thirty years) over which the issue of the nine editions extends, and the changes necessarily made in each edition in accordance with new discoveries, cause the study of this volume to have an important bearing upon the history of photography.

In the first edition the word "coloring" is used instead of "toning," and it is pointed out that when a bath of "old hypo" is used, the dark tints produced are due to the combination of sulphur with the silver of the print, forming sulphide of silver.

It is also carefully pointed out by Hardwich that, when chloride of gold is added to hypo, not only is the double salt called "sel d'or" produced, but also tetrathionate of soda, which latter salt is readily decomposed, liberating sulphur. Thus a *newly made* "coloring" bath of this kind does, it is true, color prints by a deposition of gold, but *old* baths effect the work mainly by means of sulphur. He adds that crystallized sel d'or (which is a double hyposulphite of gold and soda freed from tetrathionate) can be used for the coloring bath.*

In the second edition of Hardwich (September, 1855) the word "toning" replaces "coloring." The sulphur toning bath of old, or acid hypo, is still the first one mentioned; Le Gray's method is next given; then that of toning and fixing in one bath containing hypo and gold; and, lastly, a new method by Thomas Sutton, in which crystallized sel d'or is dissolved in water acidified with hydrochloric acid.

In the third edition of Harwich, June, 1856, sulphur toning is condemned and Sutton's acid sel d'or bath recommended for toning; but there is an important line which shows the birth of a new epoch in toning: "M. Le Gray's process is objectionable on account of the excessive overprinting required. This, however, is to a great extent obviated by a modification which the writer has seen, where an *alkaline* instead of an acid solution of the (gold) chloride is employed."

The fourth edition (April, 1857) still lays stress on the sel d'or toning bath, and it contains the first description, in print, of an *alkaline* gold toning bath. This bath was the discovery of Mr. Waterhouse, and will be described more fully later on.

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* Sel d'or was discovered by M.M. Fordos and Gelis in 1843, and was known commercially as "Gelis's salt."—W. J. H.

Alkaline toning comes strongly to the front in the fifth edition of Hardwich (1859), and a formula endorsing the use of bicarbonate of soda is given, but the sel d'or bath is still strong in the running.

The last edition of his book brought out personally by Hardwich was the sixth (1861), in which there is little change; but in the seventh (1864), edited by Dawson and Hadow, the alkaline toning bath takes a strong lead, though we are told that the method of fixing and toning in one bath is "even now sometimes followed" (p. 306). The two later editions add nothing of importance.

TONING BY OTHER METALS THAN GOLD.

It has been proposed to use such metals as palladium, iridium, etc., as toning agents; and experiments have shown that pleasing tints can be obtained by their use, but for various reasons—chiefly the enhanced expense—none of them have come into use. But with one metal—platinum—it is possible that the case may be different.

The use of *platinum* as a toning agent was first proposed by M. Caranza in the French journal, *La Lumière*, for February, 1856. A Scotchman—Burnett—experimented in the same direction in the years 1858 and 1859; and quite recently (1888) Mr. Lyonel Clark has obtained considerable success by the use of this "noble" metal.

TONING WITH PLATINUM.

The only metal which is likely to compete successfully with gold is platinum. The best salt of platinum by far for toning purposes is the "chloro-platinite of potassium," K_2PtCl_4 (not the ordinary chloride or bichloride of platinum, $PtCl_4$). Make up a stock solution of 60 grains of this salt to 2 fluid ounces of distilled water. For the regular toning bath use:

Stock solution of chloro-platinite	1 fluid drachm
Nitric acid	2 drops
Water	8 ounces

The prints are to be well washed, and are afterwards immersed or floated upon the toning solution. When the desired tone is obtained (and this bath yields tints from brown to black) they should be removed, washed in alkaline water, and fixed in hypo as usual. This method is due to Mr. Lyonel Clark; it answers better with matt-surface than with albumenized paper. By using the bath stronger (only 2 ounces of water instead of 8), much blacker tones are obtained.

Classification of Toning Processes.

We are now in a position to enumerate the various toning processes which have been practised since the discovery of photography. Having done this, we shall consider, in turn, the chemical changes upon which each process depends.

- I.—Sulphur toning
  1. By old hypo.
  2. By acid hypo.
- II.—Gold toning..
  1. By mixture of hypo and gold chloride.
  2. By sel d'or.
  3. By acid gold chloride.
  4. By gold chloride plus an alkali.
- III.—Platinum toning.
- IV.—Toning by other metals.

Alkaline Toning with Carbonates and with Borax.

Alkaline Toning with Chloride of Gold Originated by Waterhouse in 1855.—In the early days of photography—thirty or forty years ago—the Photographic Society of London did good service in appointing several committees to consider such questions as the causes of fading of prints, etc. One of the most active members of that day was Mr. T. F. Hardwich, and the first indication which we get of the use of an *alkaline* toning bath is contained in a short paper "On Gold Toning Applied to Albumenized Paper," published in the *Photographic Journal* for December 11, 1858 (p. 95). In this paper Hardwich refers to "the labors of the Printing Committee appointed by your society." It had been said that these labors "issued in nothing, and that they found all their pictures to fade." He then protests against this statement, remarking:

"I have in my hands cards on which the prints experimented on by the Printing Committee are mounted; and these cards show that although many pictures have not proved permanent, yet that others, printed in a different way, have stood severe tests.

"In examining these cards, we may take, for instance, the proofs toned by sel d'or, contributed by Mr. Shadbolt. Three months' suspension in air saturated with water has made no impression on them, and although they have been mounted more than two years since that time, they are still unaltered.

"Or, again, let us examine the condition of certain prints sent to the committee by Mr. Waterhouse, of Halifax. I have mounted one of them to show you that no perceptible difference can be made out between the two halves, although one has been subjected to the ordeal above mentioned.

"It is with reference to Mr. Waterhouse's process that I wish to address you this evening; and since it appears likely to become very popular, it may not be without interest if I describe briefly how it originated. The prints were sent to the committee by Mr. Waterhouse with the following letter, as far as my memory serves me: '*I salt the paper with a chloride dissolved in a solution of caseine, and tone the image with chloride of gold. But inasmuch as Le Gray's process eats into the picture, I modify it by using an* ALKALINE *instead of an acid solution of gold. The alkali I employ is the potassæ subcarb., and I add more or less of it according to the tint desired.*'"

The "potassæ subcarb." of the druggist is our carbonate of potash.

The "Printing Committee" referred to by Hardwich in the paper from which the above remarks are quoted was appointed at the meeting of the Photographic Society of London, on 3d of May, 1855; and its "first" (and apparently only) report is printed in the *Photographic Journal* for 21st of November, 1855. Mr. Waterhouse's prints, with his remarks as quoted by Hardwich, must therefore have been sent to that committee about the middle of the year 1855, and this is the period from which "alkaline" gold toning dates.

The Modern Carbonate of Potash Bath.—The carbonate of potash bath gives lovely warm or sepia tones. It may be made up as follows:

Chloride of gold	1 grain
Carbonate of potash	15 grains
Distilled water	10 ounces

The bath should be made up an hour or so before using.

It keeps fairly well. Dissolve the potash in the water, and add the gold last of all. The best temperature for the bath is 65 deg. Fahr.

The Carbonate of Soda Bath—Hardwich, 1857.—In the fourth edition of his well-known "Manual of Photographic Chemistry," published in 1857, T. F. Hardwich makes the first mention in print of an alkaline gold toning bath. He writes (p. 132):

> "M. Le Gray's toning process (using nothing but acid chloride of gold) is objectionable on account of the excessive over-printing required. This, however, is to a great extent obviated by a modification of the process in which an *alkaline* instead of an acid solution of the chloride is employed; 1 grain of chloride of gold is dissolved in about 6 ounces of water, to which are added 20 to 30 grains of the common carbonate of soda. The alkali moderates the violence of the action, so that the print, washed with water and immersed in the gold bath, is less reduced in intensity, and does not acquire the same *inky* blueness. On subsequent fixing in the hyposulphite, the tint changes from violet to a dark chocolate brown, which is permanent."

For the important idea of an *alkaline* gold toning bath, Hardwich was indebted to Mr. Waterhouse, of Halifax, the inventor of the generally used "Waterhouse diaphragms." This is clear from a statement contained in a paper by Hardwich in the *Photographic Journal* for 11th of December, 1858 (p, 95). In this he states that Mr. Waterhouse sent to the "Printing Committee" a set of prints toned by an alkaline solution of gold; the alkali used being carbonate of potash. Hardwich then writes: "Finding that this process was more manageable than Le Gray's, and produced very permanent pictures, I was induced, in an edition of the 'Manual of Photographic Chemistry,' * which appeared about that time, to suggest a trial of it, having previously adjusted the proportions, and substituted carbonate of soda for carbonate of potash, as a salt more easily obtainable." It was unfortunate that no mention of Waterhouse's name was made in the fourth edition of Harwich's book in 1857, but the omission was certainly not intentional, for the author was one of the most open and honorable of men.

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* The fourth edition, 1857; see p. 132.

THE MODERN CARBONATE OF SODA TONING BATH.

Chloride of gold	1 grain
Carbonate of soda (sal soda)	12 grains
Distilled water	10 ounces

The solution should be made up half an hour before it is to be used. With strong, intense negatives, possessing numerous gradations, this bath gives a rich purple-black tone.

The Borax Toning Bath.—Writing of the phosphate of soda bath in 1859,* Mr. Maxwell Lyte remarks: "180 grains of borax may be substituted for phosphate of soda with a like result." A borax bath containing a little common salt is also described by Mr. John Heywood, in the *British Journal of Photography* for the same year (p. 282).

THE MODERN BORAX BATH.

Borax	60 grains
Chloride of gold	1 grain
Distilled water	8 ounces

Warm the water to about 100 deg. Fahr., dissolve the powdered borax in it, and then add the gold. Allow to cool to 70 deg. Fahr. before using.

The borax bath is ready for use immediately it is made up; but it does not keep well, and it is preferable to only make up as much solution as will tone the prints in hand. It seems to agree specially well with the ready-sensitized papers now so largely used.

Brook's Borax Bath.—Wash the prints well in plain water.

Dissolve 90 grains of powdered borax in 15 ounces of hot water. When cooled down to, say, 75 deg. Fahr., add 1 grain of chloride of gold and shake well. This ought to tone one sheet of paper. Keep the prints moving. The borax solution must be *freshly made;* a stock solution of borax does not answer nearly so well.†

Chemical Changes in the Borax Bath.—It is not easy to follow positively the chemical changes which accompany the toning of a silver print in the "borax bath," but the following equation represents what probably takes place:

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* *Photographic News*, p, 301.

† This agrees with my own experience.—W. J. H.

$$\underset{\text{Borax}}{3Na_2B_4O_7} \underset{\textit{and}}{+} \underset{\textit{Water}}{18H_2O} \underset{\textit{and}}{+} \underset{\substack{\text{Gold}\\\text{Chloride}}}{2AuCl_3} \underset{\textit{produce}}{=} \underset{\substack{\text{Boric}\\\text{Acid}}}{12H_3BO_3} \underset{\textit{and}}{+} \underset{\substack{\text{Sodium}\\\text{Chlorate}}}{NaClO_3} \underset{\textit{and}}{+} \underset{\substack{\text{Sodium}\\\text{Chloride}}}{5NaCl} \underset{\textit{and}}{+} \underset{\text{Gold.}}{2Au}$$

The sodium chlorate, which is one of the substances produced during the above reaction, attacks the silver subchloride (the "reduction product" produced by the action of light on silver chloride) and weakens the print somewhat. Hence the necessity of over-printing to some extent when the borax bath is to be used.

Burnett adds Common Salt to the Alkaline Toning Bath (1859).—Mr. C. J. Burnett contributed to the *British Journal of Photography* for 1859 (Vol. VI., p. 175), a formula for a carbonate of soda gold-toning bath, to which he recommended the addition of "common salt, 5 to 10 grains per ounce." The reason of this he stated to be that "chloride of sodium (common salt) prevents precipitation of gold even when kept long." The addition of a little salt has since been recommended in the formulas of several workers, and doubtless with the same ideas in view—that it makes the bath keep better. Its action in this direction is doubtless due to the affinity of sodium chloride for the sodium chloro-aurate which constitutes the active ingredient of most toning baths

THE ACETATE BATH.

The Acetate Toning Bath of Hannaford and Laborde, 1859.—The first mention which we have met with of the use of acetate of soda in the toning bath occurs in the report* of a meeting of the South London Photographic Society, held more than thirty years ago, when, during the discussion of a paper on "Positive Printing," Mr. Hannaford said that "recently he had employed acetate of soda with the gold."

But the first published formula for the use of the acetate bath appears to be that of the Abbé Laborde, which was given in the *British Journal of Photography* for August 15, 1860 (p. 240).

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* *Photographic Journal* for November 15, 1859, p. 83.

"Dissolve in water	35	ounces
Acetate of soda	7½	drachms
Chloride of gold	15	grains

"The solution becomes colorless by degrees, and at the expiration of twenty-four hours it is ready for use.

"If the gold bath has been used before, its action will be slower."

By the allusion to the bath having been "used before," it appears that Laborde was acquainted with what is perhaps the most valuable property of the acetate toning bath—its *keeping qualities.* Most toning baths require using the same day that they are made up; but with proper care the acetate bath will last for years. Hence it is especially useful to that class—a large one among amateurs—who tone only a few prints at a time.

Laborde's formula would now be considered too strong; and the following may be considered as the accepted formula of the present day for the acetate toning bath:

MODERN ACETATE BATH.

Distilled water	8 ounces
Chloride of gold	1 grain
Acetate of soda	30 grains

Dissolve the acetate in the water at a temperature of 80 or 90 deg. Fahr.; add the chloride of gold to it; and use it when the temperature has sunk to about 65 or 70 deg.

If the gold chloride has not been previously neutralized, it is a good plan to add a pinch of powdered chalk to the acetate bath; it removes any free acid which may be present.

A Preliminary Bath in Salt and Water to Remove Free Nitrate.—The acetate bath is one which requires the free nitrate of silver, and indeed all the soluble salts of silver, to be removed before the print is immersed in the toning-bath. This is best done by rinsing the prints in three changes of water and then soaking them for five minutes in water to which common salt has been added in the proportion of a teaspoonful to every quart. This will redden the prints considerably; and the reddening is in itself a good thing, as it makes the subsequent changes of color more perceptible.

This salt-water bath slows the subsequent toning, and if too much salt be added toning will be rendered difficult.

After soaking in the salt-water for five minutes the prints should be again twice rinsed in plain water, when they are ready to be toned.

The acetate bath is preferred by those who like "warm" tones, by which is meant shades of rich brown with a tinge of red in them.

Keeping Powers of the Acetate Bath.—The acetate bath is a favorite with amateurs, because it can be kept ready mixed and used over and over again. Like most alkaline or neutral solutions of gold, it is affected by light, so that the bottle containing it should have two or three thicknesses of brown paper pasted round it and should be kept in a dark cool corner.

But many people make the mistake of wanting the toning bath to do too much, expecting it to tone after its gold has been exhausted. If we reckon that a grain of gold will tone a sheet of paper, we see that the limit of the toning power of the modern acetate bath, made up according to the formula given above, would be six whole-plate prints, or twenty-four quarter-plates. But if we make up a good supply of the solution—say a quart—and *add as much gold solution and water every time after using* as will make the solution up to its original measure, calculating the amount of gold to add by reckoning the number of prints toned, then there is no reason why, with proper treatment, the acetate bath should not last indefinitely. The water added should also contain soda acetate dissolved in the proper proportion. Many workers can point to acetate baths which they have had in use "for years," although it is more than probable that not a drop of the original bath, owing to the repeated renewals, remains.

Barnes' Acetate Bath.—The following is a good method of working the acetate bath, and is the formula of Mr. C. B. Barnes:*

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* *British Journal of Photography* for 1889; p. 96.

"Into a gallon stone jar break a fifteen-grain tube of chloride of gold, and add half an ounce of acetate of soda, and a small pinch of chloride of sodium (common salt); pour on this about a pint of boiling water and let it stand for an hour or so, then fill up the jar with rain or distilled water, and let it stand for at least twenty-four hours before using. When the bath is required for toning, pour into the dish just the quantity required for present use, and when the toning is completed throw the used solution away. That in the jar will keep good for years, and as no used-up or partially used-up solution is poured back, it can be used to the last drop without requiring the addition of fresh gold; added to which it cannot become contaminated by anything which might find its way into the toning dish, or that portion which has been used therein."

To this we would add the caution—be sure that your "gallon" stone jar is well glazed within, and scrupulously clean.

The acetate bath was the favorite toning bath of M. Adam Salomon, the famous French sculptor-photographer, whose work was so much admired in the "sixties." If a fresh acetate bath works slowly or with difficulty, it is a good plan to give it a start by adding two or three grains of bicarbonate of soda.

Acetate Bath Ready for Immediate Use.—Put 2 ounces of acetate of soda into an earthen jar, and break in the same jar a 15-grain tube of chloride of gold. Pour a pint of boiling water over the mixture, and stir well with a glass rod. Allow the liquid to stand for a quarter of an hour (shaking up occasionally), and then pour it into a larger vessel containing five pints of cold water. Stir well, and the bath is ready for use.

At first this bath will work very quickly, and the prints will reach the slaty-blue tint which marks the "over-toned" stage in three or four minutes. Take them out early, and you will get rich deep sepia tones. This bath is given by Mr. Geo. Bradforde in the *Photo News Year-Book* for 1881 (p. 108).

Chemical Action of the Acetate Bath.—According to Abney, the chemical changes which take place in the acetate toning bath may be expressed by the following equation:

$$\underset{\text{Gold chloride}}{2AuCl_3} \underset{\textit{and}}{+} \underset{\text{Sodium acetate}}{NaH_3C_2O_2} \underset{\textit{produce}}{=} \underset{\text{Gold}}{2Au} \underset{\textit{and}}{+} \underset{\text{Sodium}}{NaCl_3} \quad \underset{\text{Trichlor-acetate}}{C_2O_2} \underset{\textit{and}}{+} \underset{\text{Hydrochloric acid.}}{3HCl.}$$

The acetate thus combining with the free chlorine liberated from the gold chloride, and thereby preventing it from attacking the silver sub-chloride which forms the dark parts of the print.

THE PHOSPHATE BATH AND LIME BATHS.

The Phosphate Toning Bath of Maxwell Lyte (1859).—In a communication* to the Photographic Society of France, Mr. Maxwell Lyte, a well-known English amateur then residing in France, gave the following instructions for toning prints:

> "Over-print a little. Wash, first in plain and then in salt-water, for ten minutes. Make up the following toning bath:
>
> (ORIGINAL PHOSPHATE BATH OF 1859.)
>
> | | | |
> |---|---|---|
> | Chloride of gold | 15 | grains |
> | Phosphate of soda (the purified tri-basic phosphate of commerce) | 300 | grains |
> | Distilled water | 1¾ | pints |
>
> "This bath ought to be completely neutral, or at all events rather alkaline than acid."

Here, again, we should consider this bath as too strong in gold. The "phosphate bath" now generally used is made up as follows:

MODERN PHOSPHATE BATH.

Chloride of gold	1 grain
Phosphate of soda	20 grains
Distilled water	8 ounces

The tones given by this bath are of a rich purple; but the toning should be carried slightly beyond this, or until the prints are of a full violet or violet-black hue, as they "go back" somewhat during the subsequent processes of fixing and washing.

This phosphate toning-bath will keep for some little time before using, and indeed is better if made up an hour before it is required; but it cannot be used a second time, so that no more should be mixed than is required. As in all toning baths, the best plan is to dissolve the soda in the water, and

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* Reprinted in *Photographic News* for March 4, 1859, p. 301.

add the gold last of all. The bath should be quite colorless before it is used; but it ought to lose its yellow hue (caused by the addition of the gold salt) in a few minutes.

It will be noticed that Maxwell Lyte recommended bathing the prints in salt-water before placing them in the phosphate bath. This practice is not now, however, generally followed. Indeed, Abney recommends that with this "toner" a little free silver nitrate be left in the print. It is usually enough to rinse the prints in three changes of water—rapidly in the first one, and allowing two or three minutes only in each of the others—to have the prints in the best possible condition for toning in this phosphate bath.

Cause of "Measles" in Silver Prints.—Sometimes the prints, after they have been toned and fixed, show a number of small white and red specks all over their surface, producing what professional printers have termed "mealiness" or "measliness" in the prints. The cause of this is that little or no free nitrate of silver has been left in the sensitized paper. Perhaps the sensitizing bath was too weak in silver, or the paper may have been washed after sensitizing in order to make it keep better. When such paper is exposed to light (as it must be during printing) the silver chloride is decomposed into black silver sub-chloride and chlorine:

$$\underset{\text{Silver Chloride}}{2AgCl} \;\underset{\textit{produces}}{=}\; \underset{\text{Silver Sub-Chloride}}{Ag_2Cl} \;\underset{\textit{and}}{+}\; \underset{\text{Chlorine.}}{Cl}$$

The free chlorine attacks the albuminate of silver, and combines with some of its silver to form little spots of fresh silver chloride, which, being then acted on by light, is blackened in its turn, but to a slightly different tint. It is these spots or specks which produce the "measles."

The best remedy for measles is to *fume* the paper for ten minutes before printing. This is usually done by exposing the paper in a closed box having a perforated false bottom (underneath which is a saucer containing a little strong ammonia) to the fumes or vapor of ammonia; or the *pads* of the printing-frame may be fumed instead of the paper. The ammonia then combines with the chlorine as fast as the latter is liberated, and ammonium chloride is formed, which is a quite harmless substance:

$4NH_3$	+	$3Cl$	=	$3NH_4Cl$	+	N
Ammonia	*and*	Chlorine	*produce*	Ammonium Chloride	*and*	Nitrogen.

Toning with Salts of Lime.—Three of the salts of lime have been and are commonly employed in the processes of toning.

The carbonate of lime ($CaCO_3$) is usually employed in the form of powdered or "precipitated" chalk to neutralize the hydrochloric acid which is invariably present in commercial chloride of gold.

The true "chloride of lime," or calcium chloride ($CaCl_2$), is employed in certain toning baths.

Commercial "chloride of lime," or chlorinetted lime (often called "bleaching powder," and also much used for disinfecting purposes), is a *mixture* of calcium chloride ($CaCl_2$) and calcium hypochlorite ($CaCl_2O$).

Le Gray Introduces the "Chloride of Lime" Toning Bath.—Gustave Le Gray, the famous French photographer of forty years ago, was a man not unwilling to recognize improvements, even in his own discoveries. His introduction of acid chloride of gold as a toning bath about 1850 having been objected to on account of the great amount of over-printing necessary, and Waterhouse and Hardwich having shown in England (1855–8) that an *alkaline* solution of gold was preferable, Le Gray announced to the French Photographic Society early in 1859 that ordinary bleaching powder (the commercial "chloride of lime"), added to a solution of chloride of gold, made a toning bath far superior to his former acid bath. His formula* was:

Distilled water	1000 parts
Commercial chloride of lime	1 part
Chloride of gold	1 part
Chloride of sodium	1 part

This bath tones slowly but regularly, and gives black tones.

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* Reprinted from the French *Bulletin* in Sutton's Photographic Notes for 1859, pp. 41, 106.

Sutton's Lime Bath.—In Sutton's pamphlet on "Positive Printing" (1863) he writes: "The best toning bath, and that which I most strongly recommend, is a solution of a double salt of gold, called 'calcio chloride,' which consists of a combination of chloride of gold with chloride of calcium, rendered slightly alkaline by an excess of chloride of lime. This solution is as limpid and colorless as water, does not become decomposed by keeping, and is always ready for use."

Lime Bath with Chalk.—Shake up 40 grains of powdered chalk with 1 pint of *hot* distilled water. Add 2 grains of chloride of lime and shake again. Lastly, add 2 grains of chloride of gold. Shake a third time and allow to stand till cool (65 deg. Fahr.); the bath is then ready for use, though it will work much better after keeping for a day. This bath gives black tones with good negatives, and paper which is not too old.

A Modern Lime Bath.—Make up three stock solutions: (A) 15 grains of gold chloride in 7½ ounces of water; (B) ¼ pound of slaked lime (calcium hydrate, CaH_2O_2) in a quart of water; shake well and allow to stand till the excess of lime has sunk to the bottom; (C) 1 ounce of dry calcium chloride dissolved in 1 quart of water. To make up the toning bath, take ½ ounce of the chloride of gold solution and shake it up in 3 ounces of water; add to this the B solution (lime-water) until the color of a bit of red litmus paper placed in it is just changed to blue; then add ½ ounce of the C solution, shake well, and the bath is ready for use.

The Bicarbonate Toning Bath.—Bicarbonate of soda was used in a complicated "toning and fixing" bath by M. Jobard,* in 1859. In November of the same year Mr. John Heywood gave a formula in the *British Journal of Photography*, p. 282, in which he recommends the prints to be well washed in both plain water and salt water, and then a bicarbonate toning solution to be laid on with a brush in a manner which we shall describe further on.

In 1863 Mr. G. Spiller gave the following formula for a bicarbonate bath in a paper which he read* before the Photographic Society of London:

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* See *Bulletin de la Société Francaise de Photographie* for 1859; translated in *Photographic Journal* for same year, p. 8.

Chloride of gold	5 grains
Bicarbonate of soda	20 grains
Water	1 pint

All these old toning baths err in being too strong in gold.

THE MODERN BICARBONATE BATH.

Chloride of gold	1 grain
Bicarbonate of soda	5 grains
Distilled water	10 ounces

This bath is ready for use ten minutes after it is made; but it will not keep.

The Tungstate Bath.—A formula given by Mr. A. Hughes, in 1865,† reads: "Take the chloride of gold and just neutralize with tungstate of soda, and then to each grain of gold add 20 grains of the tungstate; dilute with boiling *distilled* water, and when cool the bath is ready for use. Distilled water is mentioned, as common waters vary so much that they sometimes upset all formulas. In strengthening this toning bath, the gold may be simply neutralized with the tungstate, the excess not being required. This bath can be kept and strengthened from day to day, as required, *ad infinitum.* It is found to tone to a rich purple one and a quarter sheets of paper with 1 grain of chloride of gold."

MODERN TUNGSTATE BATH.

Tungstate of soda	20 grains
Chloride of gold	1 grain
Boiling water	8 ounces

Ready for use as soon as cold. Add more gold, with a grain or two of tungstate, at the end of each day's work.

Carbonate of Magnesia Toning Bath.—In April, 1866, Mr. E. Seeley read an account of a gold toning bath containing carbonate of magnesia before the North London Photographic Association,‡ in which he emphasized the following points:

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* *Photographic Journal*, vol. viii., p. 410.

† *British Journal of Photography*, p. 206.

‡ *Photographic News*, 1866, p. 173.

The gold chloride should first be neutralized (as sold it is always acid) by the addition of a little carbonate of soda or powdered chalk.

The carbonate of magnesia should be well shaken up with warm (80 deg. Fahr.) distilled water. In this it is only slightly soluble, 50 ounces of water dissolving only 1 grain. The solution is then alkaline to test-paper. Let the solution stand and then pour off the clear part. Add 1 grain of gold chloride to every 20 ounces of the clear solution. The toning bath so prepared is ready for use after twenty-four hours. It will keep well for several days, but slowly loses its power after that. When used it should always be *slightly* alkaline to test-paper.

When using this "magnesia" bath the prints should *not* have all the free nitrate of silver washed out of them. The last wash-water used should be decidedly milky.

This bath requires a well-silvered paper, and would therefore be of little use with much of the ready-sensitized cheap paper of the present day, most of which is sensitized by floating on a bath containing only about 30 grains of silver nitrate to the ounce of water. The best proportion is double this amount, or from 50 to 60 grains to the ounce.

Seeley claimed that with the carbonate of magnesia bath "at least five sheets of paper of the full size can be toned with one grain of the chloride of gold. We usually tone six and sometimes seven." It gives black tones.

The Benzoate Bath.—In 1864 Mr. Carey Lea described a benzoate of potash toning bath in the *Philadelphia Photographer*, which he considered gave even better tones than the acetate bath. He writes: "Three or four grains of caustic potash are dissolved in water in a glass vessel, and the solution is supersaturated with benzoic acid. The exact quantity of the acid is unimportant, provided that rather more than enough to saturate the alkali is added. The first portions of acid dropped into the potash dissolve instantly by combining with the potash, and when a fresh addition refuses to dissolve after a few moments, it may be concluded that enough has been added. The solution is then to be warmed till the remaining acid dissolves. Three or four grains of chloride of gold in solution are then added; and the whole diluted so as to form a bath of eight to twelve ounces."

Lea adds that the bath so prepared may either be used at once, or will keep well.

INVESTIGATIONS OF SUTTON, AND OF DAVANNE AND GIRARD INTO TONING PROCESSES.

Thomas Sutton on Toning in 1859.—Few men held more decided ideas upon photographic matters than Thomas Sutton, who edited *Photographic Notes* from 1856 to 1868.

In his periodical for September 1, 1859 (Vol. IV., p. 217), Sutton speaks very clearly and correctly on the subject of toning:

"About the year 1851 M. Le Gray published a method of gold toning in which *chloride of gold, rendered acid by the addition of muriatic acid*, was used. The print being first greatly over-printed, was washed and then put into this bath, where it was quickly bleached and toned. It was then washed and fixed in fresh hypo as usual. No chemical reason was given for *acidifying* the chloride of gold, and it now appears that this was wrong; and that it ought to have been made alkaline instead of acid. Hundreds of thousands of prints have been lost through this mistake, for had M. Le Gray given the right formula at first, most persons would probably have employed it.

"I first saw the account of this toning process in Mr. Hennah's translation of Le Gray's formula, and tried it, but it entirely failed. Then I thought it possible that sel d'or might be the right thing, and that Mr. Hennah had by mistake translated it into chloride of gold. So I got some *sel d'or*, and it answered perfectly, except that the prints did not require over-printing. Then I worked away with the sel d'or process upon plain paper—added serum of milk to the salt to give vigor—and washed the prints with ammonia to decompose the free nitrate into ammoniacal oxide of silver. After some months of experimenting I sent an account of the sel d'or process to the *Photographic Journal*, and it attracted the attention of Mr. Hardwich, and was thought a useful novelty.

"But the sel d'or process did not answer upon albumenized paper, and that was all the rage; so albumenized prints were toned in a bath of hypo to which chloride of gold was added; and they have for the most part faded. I would observe here that I have known many sel d'or prints fade in consequence of the following improper treatment: The acid sel d'or is not thoroughly washed out of the print before putting it into hypo; then the acid makes the hypo milky, and the print is sulphurated, and therefore fades. But when the sel d'or process is properly conducted the prints do *not* fade. Not one of my own sel d'or prints have faded.

> "And now comes the funny part of this history. Someone tried *alkaline* chloride of gold instead of Le Gray's acid mixture, and it was found to answer capitally, particularly upon albumenized paper. It was not until after years of beating about the bush, and after French and English chemists had exhausted their resources, and a Printing Committee had acknowledged itself beaten by the difficulty of the problem, that the happy thought occurred to some one of trying *alkaline* instead of *acid* chloride of gold. The result is that it answered and solved the problem, and no difficulty now remains in getting permanent gold-toned albumenized sun-prints."*

Sutton then proceeds to give directions for making and using a toning bath of alkaline chloride of gold in a manner which is practically identical with the mode employed at the present day:

> "Take the common acid chloride of gold, containing hydrochloric acid in excess. Dissolve it in water, about half a grain to the ounce. Then dissolve a little carbonate of soda in distilled water (the strength is immaterial). Put a strip of litmus paper into the gold solution; it is quickly reddened; then add the soda solution drop by drop until the blue color is restored to the litmus paper. This is the toning bath—and the mode of using it is as follows:
>
> "After removing the print from the pressure-frame wash it thoroughly in several changes of water, in order to remove the free nitrate of silver. This washing is very important, for if nitrate of silver is introduced into the toning bath it throws down chloride of silver and metallic gold, and of course destroys the bath.
>
> "Then put the print into the toning bath. It quickly takes the well-known deep purple color due to gold; but the *time* depends upon the strength and temperature of the bath. With a fresh bath the print is toned in about a minute. The lights do not become yellow, but on the contrary are bleached; and if the print is left too long in the bath they assume a dull white, which reminds one of putty, at the same time that the blacks get too black; and the print has a sombre disagreeable look.
>
> "When the print has been toned, wash it well in several changes of water, and then put it into a fresh hypo bath rendered alkaline by the addition of a little carbonate of soda or ammonia."

The above contribution from the popular pen of Sutton doubtless helped materially to introduce alkaline gold toning. But the Rev. W. H. Burbank, in his book on "Photographic Printing Methods," is hardly correct when he writes (p. 46):

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*Alas! Thomas Sutton, we fear you were a little "too previous" in making this statement. We wonder how many of these prints made in 1859 are now in existence unchanged? Not many.—W. J. H.

"Hence, the sel d'or bath, as the mixed bath was termed, was soon discarded in favor of alkaline solutions of chloride of gold, first introduced under the name of Sutton's Alkaline Toning Bath." To begin with, the "sel d'or" bath is not the same as the "mixed bath"; while the introduction of the alkaline method is due in the first place to Waterhouse (1855), and secondly to Hardwich (1857).

The Classical Researches of Davanne and Girard in 1863–4.—It was reserved for two French chemists and photographers—MM. Davanne and A. Girard—to publish, in 1864,* the first complete and scientific research which had been made into the theory of toning.

They begin with a definition: "The operation to which the name of *toning* is given in photography, has for its object the changing the hue of the positive proof, so as to place it in the best possible conditions of stability; and, at the same time, to impart to it an agreeable tint."

In this definition we note that toning has a *dual* object. It is not merely a coloring operation; but one in which—by replacing one metal by another—(gold ordinarily taking the place of silver) a picture possessed of greater elements of permanence is secured.

One way in which the subject of toning may be considered is under the two heads of:—

I. Toning before fixing.

II. Toning after fixing.

The latter method is to be avoided because (1) of the extra trouble involved by the thorough washing which the print would then have to undergo between the two operations; (2) because the gold, in depositing, would cause the formation of a certain amount of chloride of silver, which would blacken when the print was subsequently exposed to light; a final fixing bath would obviate this, but it would take time and cause trouble; (3) the albuminate of silver would undergo an injurious change of hue by contact with the hypo before toning.

***Researches sur les epreuves photographiques positives.* Paris: Gauthier-Villars. Translated in the *Photographic News* for 1863–4.

Considering the subject of toning from the point of view of the agent employed, we have :

I.—Sulphur Toning ; as by means of :

(*a*) Old hyposulphite.

(*b*) Acidulated hyposulphite.

(*c*) Hyposulphite charged with salts of silver.

This method is radically bad, for the presence of sulphur (as shown by Davanne and Girard in their memoir read before the French Photographic Society, 19th October, 1855) is the principal cause of the fading of silver prints.

II.—Gold Toning.—As toning by means of gold is the universally adopted method, it must be considered in detail.

Theory of Toning.—Ordinary toning is effected simply by the *substitution* of one metal for another—gold taking the place of silver. It is exactly the same as when a plate of silver is dipped into an ordinary gilding solution. Some of the silver is dissolved, and gold takes its place. It is never possible, however, to effect a *complete* exchange—the whole of the silver is never replaced by gold ; for when the outer layer of silver is replaced by gold, this gold protects the silver beneath it from further action.

Davanne's Classification of Gold-Toning Processes.—Four classes may be distinguished among the various methods of toning by means of gold which have been introduced since 1850.

(1) *Acid Gold Toning.*—By this mode commercial chloride of gold is employed, to which a certain quantity of an acid—generally hydrochloric acid—is added. This was the method practised by Le Gray. The prints are so greatly reduced by this bath that to look presentable when finished, they must be over-printed until they are nearly black all over.

(2) *Toning by Sel d'Or.*—In the *Photographic Journal* for March 20, 1855, Thomas Sutton recommends the following coloring bath :

Distilled water	30 ounces
Sel d'or (*not* chloride of gold)	15½ grains
Pure hydrochloric acid	1 drachm

This "sel d'or" is crystallized hyposulphite of gold. It answers well for prints on plain or matt-surface paper, but not for albumenized paper.

(3) *Toning with Neutral Chloride of Gold.*—The double chlorides of gold and either potassium or sodium are used in this method.

(4) *Toning with Alkaline Gold Chloride.*—The double chloride of gold and sodium is most frequently employed; and to this are added certain salts having alkaline qualities, such as the bicarbonate, acetate, etc., of soda, and chloride of lime. This method was first used by Mr. Waterhouse in 1855; but it was not published until 1857.

Chemical Analyses of Untoned and Toned Prints, performed by Davanne and Girard.—A very important feature in the work of the two French chemists whose results we are now summarizing consisted in the numerous chemical analyses which they made of toned and untoned prints.

These analyses led Davanne and Girard to the following conclusions:—

"1st.—In all toning processes, where no accessory phenomenon intervenes, the replacing of silver by gold takes place in the atomic proportions required by the nature of the salt of gold employed.

"2d.—This replacing takes place upon the portions formed of silver by simple substitution, and upon the portions formed of silver and argentino-organic matter by a double decomposition, which forms, in the place of the latter, a corresponding auric-organico compound, analogous to the combinations which take place in the process of dyeing, between the coloring materials and the organic tissues. We also believe that it is to this auric-organico combination that the proof owes all its brilliancy.

"3d.—The replacing of the silver by gold takes place equally upon the darkest portions as upon the half-tones; however, it appears to be more rapid upon the parts slightly colored, and this result is easily explained by the lesser thickness of these parts.

"4th.—The deposit of gold is also much more rapid upon a paper simply salted—the picture of which is consequently formed, for the most part, of metallic silver—than upon a paper simply albumenized, the picture of which is, consequently, almost solely formed of a sort of argentico-organic *lake*, upon which the double decomposition we have spoken of above must take place.

"5th.—A comparison of the results furnished by the four classes of toning processes we have examined above, shows (*a*) that the application of solutions of gold acidulated with hydrochloric acid cannot be performed successfully; (*b*) that the double hyposulphite of gold and soda (sel d'or),

> does not give favorable results except in presence of an excess of ammonia or by hyposulphite of soda, by which it enters the category of neutral or alkaline toning ; and (*e*) that in fact it is only in the employ of neutral or alkaline baths that we should seek the practical conditions of toning."

Most of these conclusions have been substantiated by the work of other investigators in later years.

CHAPTER XXXI.

TONING OF PHOTOGRAPHS (CONTINUED).

Modern Ideas About the Chemistry of Toning.

Meldola upon Toning.—In the admirable series of lectures on the "Chemistry of Photography," delivered at the Finsbury Technical College, London, in 1888, and reprinted as a book (published by Macmillan & Co., London, and sold by The Scovill Co.) in 1889, we get the ideas upon the chemistry of photographic toning held by one of the first of modern chemists.

When chloride of gold is dissolved in hydrochloric acid, a compound named chloro-auric acid is formed, thus:

$$\underset{\text{Chloride of Gold}}{AuCl_3} \quad \underset{\textit{and}}{+} \quad \underset{\text{Hydrochloric Acid}}{HCl} \quad \underset{\textit{produce}}{=} \quad \underset{\text{Chloro-Auric Acid.}}{HAuCl_4}$$

This chloro-auric acid is obtained in yellow crystals when the solution is evaporated. The chemical composition of these crystals is $HAuCl_4, 4H_2O$. These crystals are deliquescent, and when they are dissolved they yield an acid solution, which must be neutralized with powdered chalk before it can be used for toning.

The "chloride of gold" usually kept by dealers in photographic chemicals is not, however, the above salt, but a double salt ($NaAuCl_4, 2H_2O$), which is obtained by adding a solution of common salt to auric chloride and then evaporating the liquid to the crystallizing point. This double salt is evidently the sodium salt of chloro-auric acid, and may therefore be called sodium chloro-aurate; it is neutral and non-deliquescent.

Toning consists in so using this sodium chloro-aurate as to "deposit on the darkened portions of the unfixed print a finely precipitated powder of reduced gold, which changes the reddish color of the mixed reduction products* into the tone so familiar in finished silver prints."

To insure the neutrality of the toning bath we mix with the gold chloride various substances, such as chalk, borax, or several salts of sodium, as the carbonate, bicarbonate, or acetate.

Now gold is "reduced to the metallic state with great ease from a neutral or alkaline solution." Let ferrous sulphate, for example, be added to a ready-made toning bath, and the gold is at once precipitated as a blackish powder on the bottom and sides of the vessel in which the experiment is performed:

$2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 +$
Gold Chloride *and* Ferrous Sulphate *produce* Gold *and* Ferric Chloride *and*
$2Fe_2(SO_4)_3$
Ferric Sulphate.

Now the "reduction products" (whatever their exact nature may be) present in the untoned print are ready—and able—to play the part of reducing agents. They decompose the gold salt, and attract the gold toward themselves. The *unaltered* silver chloride, etc., possess no such power, and therefore the white parts of the print remain untoned.

Hyposulphite of soda is a powerful reducing agent, and if a very small quantity of it gets into the toning solution it will combine directly with the chloride of gold, and prevent its precipitation upon the image. Hence the fixing bath ought always to be kept at a considerable distance from the toning bath; and after the hands have touched "hypo" they should be well washed (and a brush used to dislodge any of this deleterious chemical which may have got under the finger-nails) before they are permitted to handle the prints which are in the toning bath.

Thus the toning bath may be considered "as containing a potential deposit of metallic gold ready to be precipitated on any reducing surface that may be bathed by it." The only "reducing surface" which we should allow to come in contact with the gold solution is the surface of the print which we are desirous of toning.

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* These "reduction products" are those resulting from the action of the light upon the silver chloride and silver albuminate with which the sensitized paper is coated. According to one theory they are "sub-salts" of silver; according to another, metallic silver.

Why the Toning Bath should be Prevented from becoming Acid.—Free hydrochloric acid in a toning bath acts as a restrainer, preventing the deposition of gold, or allowing it to be deposited so slowly that it appears as the *red* form of the gold molecule; whereas to change the tint of the print (which is red to begin with) we desire the molecule of gold to reflect *blue* light, and to do this the gold must be deposited more rapidly.

Now free hydrochloric acid is often present in commercial chloride of gold; and it is almost always produced during the reduction of the gold chloride by the combination of chlorine with hydrogen. Thus for example:

$$2AuCl_3 + 3H_2O = 6HCl + Au_2O_3$$

Gold Chloride *and* Water *produce* Hydrochloric Acid *and* Gold Trioxide.

This trioxide of gold is a very easily decomposed substance, and its formation is possibly always an intermediate stage between the decomposition of the gold chloride and the actual deposit of metallic gold on the print.

To neutralize the ill effects of the free hydrochloric acid is the function of the sodium acetate, carbonate, or other salt which is added to the toning solution. It effects this by combining with the hydrochloric acid, the result being the formation of a soluble chloride and of some weak acid—such as acetic acid or carbonic acid—whose presence is harmless:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2CO_3$$

Sodium Carbonate *and* Hydrochloric Acid *produce* Sodium Chloride *and* Carbonic Acid.

Why Prints Look Weak After Toning.—Almost every instruction book on photography contains a direction to "overprint," to some extent, because the image is weakened by the subsequent operations in the toning and in the fixing baths. We must now consider why a print should lose any vigor because of the chemical action of the toning bath. Abney writes:*

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* "Instruction in Photography," p. 262.

> "Supposing a (silver) print to be thoroughly washed, and immersed in a dilute solution of gold trichloride, the following phenomena would present themselves: The picture would gradually bleach, and a blue deposit would take the place of the more vigorous red image, and, on immersion in the fixing bath, the print would be of the most feeble character."

The reason of these changes is this: The chlorine (liberated) from the gold chloride would attack the silver subchloride of the print, and—while depositing metallic gold—would in reality convert the subchloride forming the image back to the state of chloride:

$$\underset{\text{Silver Subchloride}}{3Ag_2Cl} \quad \underset{\textit{and}}{+} \quad \underset{\text{Gold Trichloride}}{AuCl_3} \quad \underset{\textit{produce}}{=} \quad \underset{\text{Silver Chloride}}{6AgCl} \quad \underset{\textit{and}}{+} \quad \underset{\text{Gold.}}{Au.}$$

In this case we see that a single atom of gold has displaced *six* atoms of silver. Of course the single gold atom cannot "make as much show" as the six atoms of silver did, and the print consequently looks very much weaker after toning in such a bath than before.

For this reason we add some substance to the toning bath which shall have an equal or greater attraction for the chlorine liberated from the gold chloride than the silver subchloride has.

This brings us to the consideration of another way of classifying toning baths, viz., into—

(*a*) Toning baths in which all the free nitrate of silver is removed from the print before toning.

(*b*) Baths in which it is an advantage to leave a little free silver nitrate in the sensitized paper.

The acetate bath is a good example of the first of these divisions. Sodium acetate has a stronger affinity for the chlorine contained in the gold trichloride than the silver subchloride of the print has. Thus the subchloride is not attacked by the chlorine; and as a result there is little diminution in the depth of the print by the subsequent fixing bath.

In the ordinary "lime bath" we have what is called "chloride of lime," but which is really a *mixture* of calcium chloride ($CaCl_2$), with calcium hypochlorite ($CaCl_2O_2$). The latter of these two substances acts as a "retarder," preventing the too rapid decomposition of the gold chloride. If prints are *thoroughly* washed and placed in a bath containing nothing but gold chloride and chloride of lime, they will tone very slowly and irregularly.

If a silver print be washed but a little (so that some free silver nitrate is left in it), and placed in a solution of plain chloride of gold, the toning will be *too rapid* to be under control.

But when we get the gold, the lime, and the silver nitrate all together, then toning takes place at the proper rate and in a regular manner.

The function of the silver nitrate is to combine with the chlorine liberated by the decomposition of the gold chloride:

$$\underset{\text{Water}}{H_2O} \underset{\textit{and}}{+} \underset{\text{Silver Nitrate}}{AgNO_3} \underset{\textit{and}}{+} \underset{\text{Chlorine}}{Cl_2} \underset{\textit{produce}}{=} \underset{\text{Silver Chloride}}{AgCl} \underset{\textit{and}}{+} \underset{\text{Nitric Acid}}{HNO_3} \underset{\textit{and}}{+} \underset{\text{Hypochlorous Acid.}}{HClO}$$

Thus the chlorine is prevented from attacking the silver subchloride of the print.

MIXED AND MISCELLANEOUS TONING BATHS.

Under this head we propose to insert certain formulas for toning baths which seem to require separate mention. They include those which contain several—or at least more than one—additions to the chloride of gold; so that they cannot be properly indicated by the name of any one chemical. They are also, for the most part, "well recommended" baths; *i.e.*, they come to us vouched for by men well known in photography, and as the results of long practice. To find them we have turned over many thousands of pages of the literature of photography.

SARONY'S TONING BATH.

STOCK SOLUTION, NO. 1.

Chloride of gold	15 grains
Distilled water	2 ounces

STOCK SOLUTION, NO. 2.

Carbonate of soda	2 drachms
Distilled water	2 ounces

To tone two sheets of paper, take:

Stock solution, No. 1	1 drachm
Stock solution, No. 2	1 drachm
Warm distilled water (80 deg. Fahr.)	8 ounces

Add the gold last; and wait till the mixture is quite colorless. This bath (published in 1867) is said to give fine violet-black tones.

Bovey's Plain Toning Bath.—The bath next to be described appeared in a series of articles on "Silver Printing," contributed by Mr. W. T. Bovey to the *Photographic News* for 1868:

"Use the orange-colored sample (commercial) of gold; which is a double salt, consisting of chloride of gold and sodium.

"Keep this gold in concentrated solution, thus:

Chloride of gold	1 grain
Distilled water	1 drachm

"1st. Measure out two gallons of water (clear rain or river water if at hand; well-water should be previously boiled).*

"2nd. Measure into a jug (porcelain) 12 grains of gold; add about 1 grain of fine table-salt; and pour over the whole, $1\frac{1}{2}$ pints of boiling water; allow this to stand awhile until lukewarm; then add the 2 gallons of water previously measured out. Your bath is made, and ready for use. Go to work."

Bovey adds that this bath improves with age. It may be strengthened when needed by pouring $\frac{1}{2}$ a pint of boiling water over 4 grains of gold, to which $\frac{1}{4}$ of a grain of fine salt has been added; allow this to cool and then add it to the main toning bath. The bulk of the whole bath (2 gallons $1\frac{1}{2}$ pints) should also be kept up by the addition of pure water when necessary. The quantities given are for professional use; amateurs should commence with one-half those stated.

Again, with this bath the "free nitrate" must *not* be all washed out of the prints. This being the case it will clearly be better not to attempt to save any of the toning bath which may be thought to be not quite spent, by returning it to the main stock. Only pour out so much as is needed to tone the prints in hand, and then throw it away.

Durand's Toning Bath.—The "Year-Book" for 1876

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* Use *distilled* water, if possible, for making up every toning solution.—W. J. H.

(p. 110) contains a formula by Mr. C. Durand, for which he claims the advantages "that a stock bottle of one grain of gold to the ounce may be kept for many weeks without depositing gold in any appreciable quantity, and it may be added to water, or to the weaker solution of it which is in daily use, at a moment's notice, without danger of that form of mealiness which is often produced by the toning bath."

Chloride of gold	15 grains
Lime-water	15 ounces
Acetate of soda	3 drachms

This is the stock solution, and should be made two days before it is required for use. It should be kept in a stoppered bottle, and for use 1 ounce of it should be added to 6 ounces of water.

After use, the solution should *not* be returned to the stock bottle, but may be thrown away (if exhausted), or placed in a second bottle to which more of the stock solution should be added when it is again desired to use it.

Cherrill's Sulphocyanide Toning Bath.—Mr. Nelson K. Cherrill was well known, twenty years ago, as the partner of Mr. H. P. Robinson, and as one of the first professional photographers in England. He contributed an account of his favorite toning bath to the "Year-Book" for 1868, p. 62.

Make up the following solution:

Chloride of gold	1 grain
Sulphocyanide of ammonium	20 grains
Distilled water	2 ounces

This is the formula as given by Cherrill, but it would, of course, be advisable to make up at least eight ounces of the solution, multiplying the above quantities by four.

No over-printing is required. Wash the prints thoroughly before toning, and use the bath fairly warm—say 70 deg. or 75 deg. Fahr. "The image is first reduced, on immersion, to a foxy tone, and then it becomes strengthened, by degrees, to a series of colors; rich warm, and brilliant, ending in black." A good deal of gold is used up by this bath; about *two* grains per sheet. The bath can be used over and over again, being strengthened with gold every time after using. After toning, fix in hypo as usual.

HEISCH'S LIME TONING BATH.

> "Dissolve 1 grain of gold in one drachm of water; to this add lime-water until the blue color is just restored to reddened litmus paper. Now dissolve 8 grains of dried, but not fused, chloride of calcium in 5 ounces of water; to this add the solution of gold, stirring all the time; and, finally, add about 3 ounces more of water."

In this formula "gold" of course means chloride of gold. Heisch was an English chemist and photographer of great experience; he published this formula in 1865. Very little over-printing is required, and the prints get blacker as they dry. This bath may be used after it has been mixed twenty minutes, or on the following day. If it be not exhausted it will keep if a drop or two of acid be added (just enough to redden litmus paper), and then, when again required for use, enough lime-water must be added to neutralize this acid.

FERGUSON'S TONING BATH.

Dissolve 15 grains of chloride of gold (an ordinary "tube") in 15 ounces of lime-water (*not* chloride of lime), and add 2½ drachms of acetate of soda to the solution.

Put the mixture in an earthen pot, stand this in a saucepan containing water and put it on the fire until it boils. Keep for two days before using.

The above is the stock solution. Dissolve 4 grains of carbonate of soda in 8 ounces of water, and add to it 1 ounce of the stock solution. Keep the bath at a temperature of 70 deg. Fahr., by standing the dish containing it in a tin dish half full of water.

LEWIS'S TONING BATH.

Mr. Abel Lewis (a well-known professional) gave the following toning bath in the "Year-Book" for 1879, p. 68:

Chloride of gold	2 grains
Acetate of soda	60 grains
Saturated solution of chloride of lime	8 drops
Bicarbonate of soda	1 grain
Distilled water	2 pints

He adds: "It is better to put a number of prints at once into a rather weak solution, and let them all tone slowly and gradually, than to use the gold in a more concentrated form. The prints thus toned have that rich, juicy appearance that rapid toning generally destroys."

Dunmore's Toning Bath (1887).

Print rather deeply in diffused light. Wash the prints in plain water till there is no milkiness. Then dip in very weak salt-water and wash again.

Mix the following toning bath a day or two before it is required:

Chloride of gold	1 grain
Chloride of calcium	4 grains
Acetate of soda	30 grains
Distilled water	10 grains

Immerse the washed prints, and keep them moving.

Some General Notes on Toning.—Three Common Mistakes in Toning.

(1) *Taking the print out too soon.*—If the print be removed from the toning bath at too early a stage, a sufficient deposit of gold will not have taken place. The fixing bath dissolves out the dark "reduction products," and the gold which is left is not sufficient to give "body" to the picture.

(2) *Leaving the prints in too long.*—When an ordinary toning bath is working well, the prints will usually be satisfactorily toned in from ten to twenty minutes. If they be left in the bath for, say, twice this time, their tone after fixing will be a slaty blue, and they will have a feeble and "washed-out" appearance. The reason is that nearly all the silver in the print has been replaced by gold. Now it is to the combination of hues afforded by the dark ruddy silver underneath, covered over by a layer of bluish gold, that we owe the fine purplish-black tones which are esteemed by most connoisseurs. But the gold *alone*, or nearly alone, is unable to produce so good an effect.

(3) *Using a Toning Bath too Strong in Gold.*—If too much gold is used in the toning bath, we get the same bluish feeble prints as described in the last paragraph, and from the same cause—too complete a replacement of the silver by the gold. Our aim in toning must be to coat or gild the silver, and not to entirely substitute the gold for it; for, although the prints might in the latter case be more permanent, still a pleasing tone must be our first, though not our only aim. As a rule, the toning bath should not contain more than one grain of gold to ten ounces of water.

TONING WITH A BRUSH.

Where it is desired to experiment on the properties of a toning solution, the method of toning with a brush will be found very economical. Wet a piece of clean white paper the size of the print, and lay it upon a sheet of glass; place the print to be toned upon this white paper, face upwards. Put a little distilled water in a test-tube, and add a drop or two of a solution of carbonate of soda, so that the liquid just turns red litmus paper blue. Then add *one drop* of a solution of chloride of gold;* apply this solution to the print by means of a camel-hair brush. If the print is a very large one, of course a larger vessel than a test-tube may be used to contain the toning solution, which, in such a case, might be applied by the broad brush called "Blanchard's brush," which is made by fastening a strip of swan's-down calico or Canton flannel to the end of a strip of glass of the desired width, the material being bent over or wrapped round the end of the glass; or a "Buckle's brush" may be used, which is made by drawing a tuft of cotton-wool (by means of a piece of string or a silver wire) into the end of a glass tube about half an inch wide. It will be found that the small quantity of toning solution, made up as described above, will tone well one, or even two half-plate prints. This "brush-toning" method was described by Mr. John Heywood as early as 1859.

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* The strength of this solution is not very material. We always put a fifteen-grain tube of gold into a stoppered bottle containing 7½ ounces of distilled water, and break the tube by shaking the bottle. There is then one grain of gold in each fluid ounce of this, the stock solution.

What to do with Old Untoned Silver Prints.

When silver prints are kept several days before toning, it usually happens that the whites assume a yellowish tint, which is unaffected by the subsequent processes of toning and fixing, and which mars the beauty of the finished results.

In such cases an improvement or cure can be effected by immersing the prints *before* toning in a bath containing three drachms of ammonia to a pint of water; wash the prints in a similar bath *after* toning; and a like quantity of ammonia should be added to the fixing bath.

Rules for Toning.

1. The prints to be toned should be printed slightly darker than they are meant to be when finished, and no parts should remain quite white.

2. For the acetate bath, wash the prints thoroughly (including one rinse in very weak salt-water) before toning. For the other toning baths, wash in three changes of water only (total time of washing not to exceed ten minutes).

3. Make up the toning bath with distilled water; use filtered rain-water if this cannot be obtained.

4. The toning bath must not be colder than 60 deg. Fahr. (65 to 70 deg. Fahr. best—test with thermometer); it must also be neutral or slightly alkaline, slowly turning red litmus paper blue; an excess of the alkali is, however, to be avoided.

5. Immerse each print separately in the toning solution. Do not tone more than six prints at a time, and frequently move the prints about, placing the bottom print on top, and so on. Rock the dish frequently.

6. *Trim* the prints *before* toning.

7. Wash the prints in three or four changes of water *after* toning.

8. Remember that good and black tones can only be obtained from really good negatives. Be content with brown tones from thin or poor negatives.

9. Always use the same dish for toning; mark it, and never use it for anything else.

10. After your fingers have been in the hypo bath they must be well washed and brushed before being again immersed in the toning bath. A mere trace of hypo spoils the toning.

11. For ready-sensitized paper, let one of the waters in which it is washed before toning contain a little carbonate of soda (½ ounce to 1 quart).

12. In making up a toning bath always add the chloride of gold *last*, after the other ingredients have been completely dissolved. The bath must never be used until it is *quite* colorless. Keep the acetate bath at least twenty-four hours before using.

13. Judge the tone of a print by weak daylight; and look through the print, holding it up to the light.

14. Quickly rinse the prints *after* toning, and then leave them to soak in a bath of very weak salt-water (half an ounce of salt to a gallon of water); this stops the further toning, which would otherwise take place.

15. Always keep your toning baths in clean stoppered bottles having brown paper pasted round them to exclude the light.

16. Touch the sensitized surface of the paper as little as possible with the fingers, especially *before* the prints are toned. The perspiration from the skin prevents the proper action of the toning solution and causes reddish marks to appear, which are most conspicuous on the dark parts (shadows) of the print.

17. Freshly-sensitized paper is the easiest to tone and to get black tones upon. Ready-sensitized paper does not tone so easily after keeping two or three months, and it is often sensitized upon too weak a bath of silver nitrate. The borax bath gives the best results with ready-sensitized paper.

18. If the prints *blister* during or after toning, they can generally be cured by transferring the prints direct from the toning bath into a mixture of methylated spirit four parts and water one part.

19. Paper that is too *dry* will not give easily toned prints. The paper should be kept, if very dry, in a *damp* cellar, etc., for an hour or two before it is put into the printing frame.

20. Toning baths weak in gold take longer to tone the prints,

but produce better tones than baths rich in gold. Never exceed the proportion of one grain of gold to eight ounces of water; in most cases the same amount of gold to ten or twelve ounces of solution will give even better results.

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CHAPTER XXXII.

THE CHEMISTRY OF PHOTOGRAPHIC "FIXING" PROCESSES:—I. EARLY METHODS.

To begin with, we must confess that the term "fixing" is not a very correct one; and that "clearing" would better express what is here meant. When an ordinary dry-plate—coated with gelatine containing silver bromide—is exposed within the camera, and the picture impressed upon it by the lens subsequently developed, we have a great number of particles of black metallic silver forming the picture, and around and between these are white particles of silver bromide which have *not* been affected by the light. The consequence is that the developed (but unfixed) picture stands out boldly against its white background and border. But if the plate be, in this condition, exposed to daylight, the light affects the remaining particles of silver bromide, changing them also into metallic silver, or at least into a dark-colored compound indistinguishable (to the sight) from it, and thus the entire surface of the plate is blackened and all traces of the picture are lost.

Now what is called "fixing" consists in the removal of the unacted-on silver bromide from our developed dry-plates; the particles of metallic silver forming the picture being then left free from any chance of obscuration, and imbedded in the colorless gelatine by which they are caused to adhere to the glass plate. Silver prints taken from these negatives evidently also need fixing for similar reasons.

For this "fixing," what is wanted, then, is some substance which will dissolve silver bromide or chloride (thereby removing it from the gelatine film), but which has no action upon metallic silver.

It would seem that "*clearing*" would be a better name for the process than "*fixing*"; for in any case the silver remains fixed in the film. What we desire to do is to "clear" the molecules of black silver forming the picture from the surrounding silver bromide. But the term "fixing" has got into general use for the operation; and technical terms—once fairly brought into use—are very difficult to displace; even though it can be shown that they are incorrect.

Wedgwood and Davy Unable to Find a Fixing Agent.

Thomas Wedgwood, a son of the great English potter, was the first man to obtain tolerable copies of more or less transparent objects by the action of light. This he did by placing paper coated with nitrate of silver underneath paintings on glass, leaves, the wings of insects, etc. The light passing through the substance according to its transparency blackened the sensitive surface beneath, leaving it gray where it was partly protected and white where it was completely protected by the semi-transparent and opaque parts of the substance.

Sir Humphry Davy (then Professor at the Royal Institution in London) was the friend of Wedgwood (whose own health was exceedingly bad). Davy found that the chloride of silver acted rather better than the nitrate, and that it gave better results when spread upon leather than upon paper. He embodied his own and Wedgwood's experiments in a paper which was printed in the *Journal of the Royal Institution*, for 1802, which paper he winds up with the remark that—"Nothing but a method of preventing the unshaded parts of the delineations from being colored by exposure to the day is wanting to render this process as useful as it is elegant." Thus, for want of a fixing process the work of Wedgwood and Davy was rendered useless, and "photography" was postponed for nearly half a century.

Niepce "Fixes" with Petroleum.

The first man who ever obtained a permanent picture by the aid of light was Joseph Nicéphore Niepce, a patient and persevering worker in France. The key of his discovery lay in the fact that bitumen is rendered insoluble by the action of light. He coated metal plates with bitumen, which he then exposed beneath engravings, and in the camera. Then he removed the plates and washed them with a mixture of "one part, by volume, of the essential oil of lavender, and ten of oil of white petroleum." A thorough washing with water followed.

The chemical action of light upon bitumen is to cause it to combine with oxygen (from the air) and so to become hard and insoluble. But under the opaque lines of the engraving, and in the shadows of the camera-picture, the bitumen remained unoxidized and soluble; and so was washed away by the petroleum. In this way a copy of the desired object was obtained. But the time required for oxidation of the bitumen was terribly long—six hours to secure pictures in the camera—and while endeavoring to remedy this defect Niepce died, in 1833, without ever having published his results. He had, however, communicated his experiments, in 1829, to a French scene-painter named Daguerre, with whom he had entered into partnership.

"SEA-SALT" USED AS A FIXING AGENT BY DAGUERRE.

There is every reason to believe that the first fixing agent employed by Daguerre in his "daguerreotype" process was simply a strong solution of sea-salt, or common salt simply, if sea-salt could not be obtained.

Herschel's generous conduct in at once making public his knowledge of the excellent qualities of hypo as a fixing agent, enabled Daguerre to mention the latter substance in his application for an English patent for his daguerreotype process, but he mentions sea-salt first. The following extract is from Daguerre's patent specification dated 14th of August, 1839:

"*Fifth and last process.*—To remove from the plate the coating of iodine, and thus to fix the picture, a solution of sea-salt may be used, but a weak solution of hyposulphite of soda is preferred. The plate is first dipped into distilled water, then moved about in the saline solution until the yellow color of the iodine is entirely removed, again plunged into water, and finally subjected to the action of a continuous stream of hot water falling on an inclined plane carrying the plate, thus cleansing it perfectly; it is then ready for mounting by being placed in a pasteboard case, and covered with glass, thus preserving the silver surface from being touched, and from tarnishing."

Sea-salt is the solid matter left by the evaporation of sea-water, of which 100 pounds by weight contains no less than 3⅓ pounds. More than three-fourths of this solid residue is common salt (sodium chloride, $NaCl$), but there is also much magnesium chloride ($MgCl_2$), and some potassium chloride (KCl), and magnesium bromide ($MgBr_2$). These substances are each and all able to dissolve—to a certain extent, and with varying powers—the haloid salts of silver employed in photography. It is doubtful, however, if a photograph, either negative or print, was ever perfectly fixed by this means. Doubtless Daguerre knew well the imperfection of his original fixing process, and eagerly seized upon that of Herschel.

Fox Talbot Uses Potassium Iodide and Sodium Chloride as Fixing Agents.

The first public exhibition of photographs in England was on January 25, 1839, when Professor Faraday displayed some of the "Photogenic Drawings" made by Fox-Talbot, to the members of the Royal Institution of London. Beyond affirming that the pictures shown were due solely to the agency of light, Faraday said little or nothing. But a few days later—on January 31st—Talbot read a paper giving a preliminary account of his work up to that date before the Royal Society of London; and this paper was printed in the *Philosophical Magazine* for March, 1839.

Talbot's "Photogenic" process consisted in impregnating paper with silver chloride and nitrate. Although pictures *could* be obtained in the camera by a very long exposure (an hour or so) yet it was a printing process mainly.

Referring to the work of Wedgwood and Davy, published in 1802, Talbot writes*: "The circumstance announced by Davy that the paper on which the image was depicted was liable to become entirely dark, and that nothing hitherto tried would prevent it, would perhaps have induced me to consider the attempts as hopeless, if I had not (fortunately) before I read it, already discovered a method of overcoming this difficulty, and of fixing the image in such a manner that it is no more liable to injury or destruction.

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* *Philosophical Magazine* for March, 1839, vol. xiv., pp. 161-196.

"In the course of my experiments directed to that end, I have been astonished at the variety of effects which I have found produced by a very limited number of different processes when combined in various ways; and also at the length of time which sometimes elapses before the full effect of these manifests itself with certainty. For I found that images formed in this manner, which have appeared in good preservation at the end of twelve months from the time of their formation, have nevertheless somewhat altered during the second year. This circumstance, added to the fact that the first attempts which I made became indistinct, in process of time (the paper growing wholly dark) induced me to watch the progress of the change during some considerable time, as I thought that perhaps *all* these images would *ultimately* be found to fade away. I found, however, to my satisfaction, that this was not the case, and having now kept a number of these drawings during nearly five years without their suffering any deterioration, I think myself authorized to draw conclusions from my experiments with more certainty."

From this we see the extreme importance which Talbot rightly assigned to the discovery of a fixing agent. It was useless to be able to make pictures, unless those pictures were capable of being fixed or preserved. Although Talbot's first successful attempts at photography were made as early as 1834, yet (from just doubts as to the permanency of his results) he did not publish his discovery until 1839; and probably would not have done so then had not his hand been forced by the rumors of Daguerre's doings in France.

In the same paper Talbot continues:

"At the very commencement of my experiments upon this subject, when I saw how beautiful were the images which were thus produced by the action of light, I regretted the more that they were destined to have such a brief existence, and I resolved to attempt to find out, if possible, some method of preventing this, or retarding it as much as possible. The following considerations led me to conceive the possibility of discovering a preservative process.

"The nitrate of silver, which has become black by the action of light, is no longer the same chemical substance that it was before. Consequently, if a picture produced by solar light is subjected afterwards to any chemical process, the white and dark parts of it will be differently acted upon, and there is no evidence that after this action has taken place these white and dark parts will any longer be subject to a spontaneous change; or, if they are so, still it does not follow that that change will now tend to assimilate them to each other. In case of their remaining dissimilar, the picture will remain visible, and therefore our object will be accomplished.

"If it should be asserted that exposure to sunlight would necessarily reduce the whole to one uniform tint and destroy the picture, the *onus probandi* evidently lies on those who make the assertion. If we designate by the letter A the exposure to the solar light, and by B some indeterminate chemical process, my argument was this: Since it cannot be shown *a priori* that the final result of the series of processes A B A will be the same with that denoted by A B, it will therefore be worth while to put the matter to the test of experiment, viz., by varying the process B until the right one be discovered, or until so many trials have been made as to preclude all reasonable hope of its existence.

"My first trials were unsuccessful, as indeed I expected; but after some time I discovered a method which answers perfectly, and shortly afterwards another. On one of these more especially I have made numerous experiments; the other I have comparatively little used, because it appears to require more nicety in the management. It is, however, equal, if not superior, to the first in brilliancy of effect.

"This chemical change, which I call the preserving process, is far more effectual than could have been anticipated. The paper, which had previously been so sensitive to light, becomes completely insensible to it, insomuch that I am able to show the Society specimens which have been exposed for an hour to the full summer sun, and from which exposure the image has suffered nothing, but retains its perfect whiteness."

After reading these paragraphs one can only exclaim; "Bravo, Talbot! spoken like a scholar and a philosopher." Davy's failure did not daunt him, and by the aid of mathematics (Talbot graduated with high honors at Cambridge University in 1821) he is able to demonstrate that a fixing agent is not an impossibility, and he goes for it.

To continue our quotations from this epoch-making paper of 1839:

"*On the Art of Fixing a Shadow*—The phenomenon which I have now briefly mentioned appears to me to partake of the character of the marvellous, almost as much as any fact which physical investigation has yet brought to our knowledge. The most transitory of things, a shadow, the proverbial emblem of all that is fleeting and momentary, may be fettered by the spells of our 'natural magic,' and may be fixed for ever in the position which it seemed only destined for a single instant to occupy.

"This remarkable phenomenon, of whatever value it may turn out in its application to the arts, will at least be accepted as a new proof of the value of inductive methods of modern science, which by noticing the occurrence of unusual circumstances (which accident, perhaps, first manifests in some small degree), and by following them up with experiments, and varying the conditions of these until the true law of nature which they express is apprehended, conducts us at length to consequences altogether unexpected, remote from usual experience, and contrary to almost universal belief. Such is the fact, that we may receive on paper the fleeting shadow, arrest it there, and in the space of a single minute fix it there so firmly as to be no more capable of change, even if thrown back into the sunbeam from which it derives its origin."

In this, his first paper, Talbot describes his results only, and gives no details as to his methods for obtaining them. But two months later* he supplied this want in the form of an "open letter" addressed to S. H. Christie, Esq., the Secretary of the Royal Society. He says that "the subject naturally divides itself in two heads, viz., the preparation of the paper, and the means of fixing the design."

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* *Philosophical Magazine* for March, 1839, pp. 209-211.

It is the latter only of these topics which concerns us at present.

"*Method of Fixing the Image.*—After having tried ammonia, and several reagents, with very imperfect success, the first thing which gave me a successful result was the iodide of potassium much diluted with water. If a photogenic picture* is washed over with this liquid, an iodide of silver is formed which is absolutely unalterable by sunshine. This process requires precaution, for if the solution is too strong, it attacks the dark parts of the picture. It is requisite, therefore, to find by trial the proper proportions. The fixation of pictures in this way, with proper management, is very beautiful and lasting. The specimen of lace which I exhibited to the Society, and which was made five years ago, was preserved in this manner.

"But my usual method of fixing is different from this, and somewhat simpler, or at least requiring less nicety. It consists in immersing the picture in a *strong* solution of common salt, and then wiping off the superfluous moisture and drying it. It is sufficiently singular that the same substance which is so useful in giving sensibility to the paper† should also be capable under other circumstances, of destroying it; but such is, nevertheless, the fact.

"Now, if the picture which has been thus washed and dried, is placed in the sun, the white parts color themselves of a pale lilac tint, after which they become insensible. Numerous experiments have shown to me that the depth of this lilac tint varies according to the quantity of salt used, relatively to the quantity of silver. But by properly adjusting these, the images may, if desired, be retained of an absolute whiteness. I find I have omitted to mention that those preserved by iodine are always of a very pale primrose yellow, which has the extraordinary and very remarkable property of turning to a full gaudy yellow whenever it is exposed to the heat of a fire, and recovering its former color again when it is cold."

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* A "photographic print" as we should style it.—W. J. H.

† Talbot's "photogenic paper" was prepared by dipping it first into a weak solution of common salt, and then into a solution of nitrate of silver so as to have *a slight excess of the latter substance.*

We have quoted Talbot's descriptions somewhat fully, as the original is likely to be inaccessible to most of our readers, and his words have not, we believe, been previously reprinted in any photographic journal. It is always better to get face to face with "the man who did it," and to read his own words rather than a paraphrase of them.

Of course, not one of Talbot's early pictures could have been properly "fixed" in the sense in which we understand the term. Some of the silver was no doubt washed out of the paper, and what was left was prevented from blackening on exposure to light by the presence of an excess of a haloid salt, either potassium iodide (KI), or common salt (sodium chloride, $NaCl$).

Talbot's first or "photogenic" method must be carefully distinguished from his "calotype" process which he patented in 1841. The former consisted of silver *chloride* upon paper; the later of silver *iodide*. The image on the former was *printed out*; on the latter it was *developed*.

Talbot also mentions that he sometimes used potassium bromide (KBr) as a fixing agent.

FIXING WITH AMMONIA BY FYFE AND OTHERS.

We have seen that Talbot attempted to use ammonia as a fixing agent for his "photogenic drawings," but with very indifferent results.

Immediately after the publication of Talbot's paper, Dr. Andrew Fyfe, Vice-President of the Society of Arts, Edinburgh, appears to have experimented on the subject, and he read some account of his results to the Society of which he was an officer, on March 27, and April 10 and 17, 1839. This paper—which is an important one—was published in the *Philosophical Magazine* for the same year. The following quotations will prove that Dr. Fyfe was an original and earnest worker:

Preservation of the Impressions.

"It is evident that, as the impression is produced by the agency of light on the compound of silver, when the paper is again exposed, the light will begin to act, and ultimately darken the whole, thus effacing the impression; hence the necessity of a preservative process. Two methods have been recommended by Mr. Talbot as applicable to the chloride, one by the iodide of potassium, the other by sea-salt. When solution of iodide of potassium is added to that of lunar caustic,* a yellow iodide of silver is thrown down. The same is the case when the iodide is put on paper, previously covered with the chloride, and, provided the solution is strong, it acts also on the chloride when darkened, thus converting it to yellow iodide, which is not in the least affected by light; hence, by putting the paper with the impression through a solution of the iodide, provided it is weak, the white chloride only is acted on, and being converted to iodide, it is no longer liable to change. As, however, the iodide will act on the dark chloride, it is of the utmost consequence to attend to the strength of the solution, which should be such that it will not attack the faint parts of the impression. After the paper is passed through it, it should be kept for some time in water to wash off the superfluous iodide of potassium, which, if left on, would gradually destroy the whole of the impression; indeed, even with this precaution, I find it extremely difficult to preserve them.

"The second method recommended by Mr. Talbot is merely immersing the paper in solution of sea-salt. This process does not, however, seem to answer well; I have repeatedly failed in preserving the specimens in this way, and even when they are preserved they are completely altered in their appearance and deprived of their original brilliancy.

"I have already stated that I prefer the *phosphate* of silver for taking the impressions, not only because it is equally sensitive as the chloride, but gives a greater variety of shades. In addition to these it has another advantage: the impressions are easily preserved. After various fruitless attempts I at last found that the darkened phosphate is not soluble in ammonia, though, as is well known, the yellow phosphate is easily dissolved. I had, therefore, recourse to this for their preservation, and though I did not completely succeed at first, yet at last I did so by attending to the precaution of washing off the ammoniacal solution; because, when left on, the impression gradually becomes darker and darker, and is ultimately destroyed, owing to the action of the light on it. The method I now follow is to put the paper into a diluted solution of water of ammonia (one of the spirit of hartshorn to about six of water) and leave it there till the yellow parts become white, showing that the phosphate is dissolved, after which it is washed with water to carry off the whole of the ammoniacal solution. It should then, when nearly dry, be subjected to pressure till dried, by which it is prevented from wrinkling, and the impression retains its original sharpness, which, unless this is done, it is apt to lose, by the fibre of the paper being raised by the repeated moistening.

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* Nitrate of silver.—W. J. H.

"Though the phosphate specimens may be preserved in this way, yet they do not retain exactly their original appearance. Those parts, whitened by the ammonia, gradually acquire a faint reddish tinge—but, though altering the appearance, it does not affect the brilliancy; indeed, in some cases, it rather improves it, by giving it a pleasing tint, which contrasts well with the darker parts, and gives the appearance of coloring. I have also found that carbonate of ammonia answers equally well, and, being much cheaper, it will of course be preferred. I generally employ a solution prepared by dissolving one part of the salt in about four of water, in which the paper is kept for a minute or so, and then afterwards washed, and subjected to pressure, as already noticed. Impressions thus preserved acquire the same reddish tinge as those acted on by ammonia.

"I have before stated that the paper may be prepared by washing it over with a solution procured by adding nitrate of silver to carbonate of ammonia. The impressions taken with that paper are easily preserved, by merely washing them with water, to carry off the part not acted on by the light, which is another advantage, in addition to those stated, for using the carbonate solution. Like the phosphate specimens, they also acquire a reddish tint.

"Other preservative methods have been recommended, as, by covering the impressions with yellow color, to prevent, as much as possible, the transmission of the chemical ray of the light; but those above stated, particularly where the phosphate or carbonate is used, are so simple and efficacious that it is unnecessary to allude to them."

Dr. Fyfe's name and work are well worth preserving. He must have been among the first—was probably *the* first—to practise photography in Scotland. His fixing process with ammonia was better than any fixing method discovered by Talbot. Silver *chloride* is freely soluble in ammonia, but not silver iodide or silver bromide. Thus ammonia can only be used for fixing prints.

Another early experimenter—J. C. Constable—arrived at the same result as Fyfe. The following letter from Constable appeared in the June number of the *Philosophical Magazine* for 1839:

"Mr. Fox Talbot, in his paper on photogenic drawing, states, that he did not succeed in preserving the drawings by means of ammonia; some experiments which I have made lead to a different result. I find that the drawings, after being soaked for some minutes in a moderately strong solution of ammonia, and then washed in clean water, withstand the action of the light perfectly, and indeed are improved by it; for the first action of the ammonia is to make the dark parts of a reddish hue, which, on exposure to the light, become again of a dark color, the light parts being unaffected. This mode of preservation has, I conceive, advantages over those already used. Common salt never preserves completely so as to enable the drawing to withstand the action of the sun.

"Iodide of potassium seems to require great delicacy of management, as when at all too strong it eats out the fainter tints, and is moreover subject to this inconvenience—that sometimes the drawings so preserved, even when kept in the dark, become entirely bleached and lose all traces of the dark lines. This at least has happened to some drawings so prepared by a friend of mine. There is no doubt that the hyposulphite of soda is an excellent preservative, but it is a salt not easily prepared, and not likely to be in the hands of those who may wish to make experiments on the subject."

Hypo at that time cost a guinea a pound, and was with difficulty procurable even at that price. For several years afterwards its price did not fall below six shillings per pound. It is now sold, in bulk, at about the same price per hundredweight! The early experimenters deserve our hearty sympathy. They had difficulties to contend with that we know nothing of. Photography was then an infant science, and the first workers had to painfully grope their way in the dark, and to first invent and then manufacture the apparatus they employed; pure chemicals were almost unattainable, and their price was prohibitive. Surely every worker of to-day ought to feel a deep interest in the way in which the foundation stones of photography were laid, half a century ago.

The powerful odor of ammonia, together with the announcement by Herschel of the splendid "fixing" powers of hyposulphite of soda, prevented the "volatile alkali"* from coming into use for fixing photographs. But its claims have been recently revived by Mr. R. H. Bow.† He states that the advantages of ammonia are: (1) Shortness of the time consumed between the toning bath and the finishing of the print, which may be less than ten minutes; (2) freedom of the print from any sulphur compounds, and consequent promise of permanency; (3) great saving of water required for the washings; (4) preservation of fainter shadings, which become bleached to a great extent under treatment with the hyposulphite; (5) the cost may be less if the ammonia and dissolved chloride of silver and other silver compounds be recovered by partial distillation and treatment with hydrochloric acid; (6) the paler shadings in the picture retain a warmer tint than in the hypo-fixed prints. This, in many cases, will be thought by some an advantage, as in portraits and sunny landscapes.

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* A chemical term for ammonia.—W. J. H.

† *British Journal of Photography* for April 15, 1887.

For fixing, almost any strength of ammonia may be used, from a 10 per cent. solution to one which is forty times weaker. The only difference is in the time required. The best plan is to use two baths—the first, say, a 2 per cent. solution, and the second bath half this strength only—and allow the prints to remain for five minutes in the first bath and for ten minutes in the second. A final washing in water for ten minutes should be given.

This ammonia fixing bath is well worth a trial; it is, indeed, to be recommended where the time is very limited.

CHAPTER XXXIII.

THE CHEMISTRY OF "FIXING" PROCESSES (CONTINUED).—II. "HYPO," "CYANIDE," AND WATER AS FIXING AGENTS.

"HYPO" AND HERSCHEL.

The claims of Sir John Herschel to a high position among the "fathers of photography" have scarcely received full recognition. It is greatly to be regretted that the Herschel family has never thought fit to prepare, or to aid others in preparing, a full biography of either Sir John Herschel or his father, Sir William Herschel. But the following extracts from one of Sir John's private note-books will show what he had done before the publication of anything about the photographic processes either of Daguerre or of Talbot. At that time rumors, but rumors only, were spread about that pictures had been obtained by some secret method by which objects were caused to "draw their own likeness"; but Talbot's first description of his own method was only made to the Royal Society on January 31, 1839, while Daguerre's account of his process did not appear until August of the same year.

Herschel's Note-Book.—"Experiment 1012, made January 29, 1839. Experiments tried within the last few days since hearing of Daguerre's *secret*, and also that Fox Talbot has got something of the same kind." (Here follow some trials of the relative sensitiveness to light of the nitrate, carbonate, acetate, and chloride of silver.)

"Experiment 1013.—Daguerre's process: Attempt to imitate. Requisites—1st, very susceptible paper; 2d, very perfect camera; 3d, means of arresting further action.

"*Tried hyposulphite of soda to arrest the action of light by washing away all the chloride of silver or other silvering salt; succeeds perfectly.*

"Papers half acted on, half guarded from the light by covering with pasteboard, were withdrawn from sunshine, sponged over with hyposulphite, then washed in pure water, dried, and again exposed. The darkened half remained dark, the white half white, after any exposure, as if they had been painted with sepia.

"January 30, 1839.—Formed image of telescope with the aplanatic lens, and placed in focus paper covered with carbonate of silver. An image was formed in white on a sepia-colored ground, which bore washing with hyposulphite of soda, and was then no longer alterable by light. Thus Daguerre's problem is so far solved.

"Experiment 1014, January 30th.—Tried transfer of print and copper-plate engraved letters."

It may be objected that these were private notes; but on March 14, 1839, Sir John Herschel read a paper before the Royal Society of London, from the published abstract of which the following quotation is taken:

"Confining his attention in the present notice to the employment of chloride of silver, the author inquires into the method by which the blackened traces can be preserved; which may be effected, he observes, by the application of any liquid capable of dissolving and washing off the unchanged chloride, but leaving the reduced oxide of silver untouched. These conditions are best fulfilled by *the liquid hyposulphites.*

"Twenty-three specimens of photographs made by Sir J. Herschel accompany his paper, one a sketch of his telescope at Slough."

Concerning this abstract of his paper, Sir John Herschel wrote, a quarter of a century later (viz., in 1864): "This is the image above mentioned as having been taken on January 30, 1839, and was, I believe, the first picture ever *fixed* for an optical image ever taken in this country—at least I have heard of none earlier. At the time of making these experiments, as already mentioned, I had no knowledge of M. Daguerre's process further than the mention of the existence of *a process* (a secret one) in a note from Admiral (then Captain) Beaufort, some time about January 23, 1839. Of course I used *paper*, not silver, and it was not a *suggestion*, but a regular uniform *practice* to use the hyposulphite; I never used anything else."

It was not likely that Herschel would use "anything else," for he was the first to call the attention of chemists to the hyposulphites and to their peculiar power of dissolving the salts of silver. It is true that hyposulphite of soda was prepared by Chaussier as early as 1799, but Herschel was the first to properly study this salt and the acid from which it was derived. His paper "On the Hyposulphurous Acid and Its Compounds," which appeared in Brewster & Jamieson's *Edinburgh Philosophical Journal* for 1819, contains the following passages:

"One of the most singular characters of the hyposulphites is the property their solutions possess of dissolving chloride of silver and retaining it in considerable quantities in permanent solution.

"*Hyposulphite of Potash.*—It dissolves chloride of silver, even when very dilute, with great readiness.

"*Hyposulphite of Soda.*—Chloride of silver newly precipitated dissolves in this salt when in a somewhat concentrated solution in large quantity, and almost as readily as sugar in the water.

"*Hyposulphite of Strontia.*—Like the rest of the hyposulphites it readily dissolves chloride of silver, and alcohol precipitates it as a sweet syrup.

"*Hyposulphite of Silver.*—Chloride of silver newly precipitated is soluble in all liquid hyposulphites, and, as before observed, in that of soda with great ease and in large quantities. This solution is not accomplished without mutual decomposition, as its intense sweetness proves—a sweetness surpassing that of honey, and diffusing itself over the whole mouth and fauces, without any disagreeable or metallic flavor."

Second and third papers from Herschel's pen on the same subject appeared in the same periodical for 1819. In the second paper he states that the chemical affinity of hyposulphurous acid for silver is so great that oxide of silver readily decomposes hyposulphite of soda, and even caustic soda—"the only instance, I believe, yet known of the direct displacement of a fixed alkali in the wet way by a metallic oxide.

"*Hyposulphite of Ammonia and Silver.*—Its sweetness is unmixed with any other flavor, and is so intense as to cause a pain in the throat. One grain communicates a perceptible sweetness to 30,000 grains of water."

Writing in 1864, Herschel remarks as to these discoveries made by him nearly half a century previously:

"The very remarkable facts then described, I have reason to believe, attracted a great deal of attention at the time, and thenceforward the ready solubility of silver salts, usually regarded as insoluble, by the hyposulphites, was familiar to every chemist. It would not, therefore, be surprising if Daguerre tried it to *fix* his plates (*i.e.*, to wash off the iodide coating); but I have been informed, though I cannot cite a printed authority for it, that at first he fixed with a strong solution of common salt. For my own part, the use of the hyposulphites was to myself the readiest and most obvious means of procedure, and presented itself at once. My earliest experiments were made in January, 1839."

HYPO ADOPTED BY DAGUERRE AND BY TALBOT AS A FIXING AGENT.

The superiority of Herschel's fixing method was patent to all; and after his publication of it in the spring of 1839 it was adopted both by Daguerre and by Fox Talbot.

In Daguerre's English patent (August 14, 1839), he says: "*Fifth and last process.*—To remove from the plate the coating of iodine, and thus to fix the picture, a solution of 'sea-salt' may be used; but a weak solution of hyposulphite of soda is preferred. The plate is first dipped into distilled water, then moved about in the saline solution until the yellow color of the iodine is entirely removed, again plunged into water, and finally subjected to the action of a continuous stream of hot water falling on an inclined plane carrying the plate, thus cleansing it perfectly."

The first book ever written on photography is Daguerre's "History and Practice of Photogenic Drawing," which was translated from the French by J. S. Memes, and published in England towards the end of 1839 (the preface is dated September 13th). On page 65 we find: "FIFTH OPERATION; *Fixing the Impression.* The object of this final process is to remove from the tablet the coating of iodine, which continuing to decompose by light would otherwise speedily destroy the design when too long exposed. For this operation the requisites are:

"A saturated solution of common salt; or a weak solution of hyposulphite of pure soda.

"The apparatus represented, Plate VI., Fig. 4, first and second views. Two square troughs, sheet copper, Plate VI., Fig. 2, both views.

"A vessel for distilled water, Plate VI., Fig. 5.

"In order to remove the coating of iodine, common salt is put into a bottle with a wide mouth, which is filled one-fourth with salt and three-fourths with pure water. To dissolve the salt shake the bottle, and when the whole forms a saturated solution, filter through paper. This solution is made in large quantities beforehand, and kept in corked bottles.

"Into one of the square troughs pour the solution, filling it to the height of an inch; into the other pour in like manner your water. This solution of salt may be replaced by one of hyposulphate* of soda, which is even preferable, because it removes the iodine entirely, which the saline solution does not always accomplish, especially when the sketches have been laid aside for some time between the fourth and fifth operations. It does not require to be warmed, and a less quantity is required.

"First, the plate placed in common water, poured into a trough, plunging and withdrawing it immediately,—the surface merely requiring to be moistened—then plunge it into the saline solution, which latter would act upon the drawing if not previously hardened by the washing in pure water. To assist the effect of the saline solutions, the plate is moved about in them by means of a little hoop of copper wire, Plate VI., Fig. 3. When the yellow color has quite disappeared, the plate is lifted up with both hands, care being taken not to touch the drawing, and plunged again into the first trough of pure water.

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* I have preserved this venerable misprint of *ate* for *ite*, because it was probably the first ever made.—W. J. H.

"Next, the apparatus, Plate VI., Fig. 4, two views, and the bottle, Fig. 5, having been previously prepared, made very clean, and the bottle filled with distilled water, the plate is withdrawn from the trough, and being instantly placed upon the inclined plane, Plate VI., Fig. 4, distilled water, hot but not boiling, is made to flow in a stream over its whole surface, carrying away every remaining portion of the saline wash.*

"Not less than a quart of distilled water is required when the design is of the dimensions indicated in the engraving, 8½ by 6½ inches. The drops of water remaining on the plate must be removed by forcibly blowing upon it, for otherwise in drying they would leave stains on the drawing. Hence also will appear the necessity of using very pure water, for if in this last washing the liquid contains any admixture of foreign substances, they will be deposited on the plate, leaving behind numerous and permanent stains. To be assured of the purity of the water, let a drop fall upon a piece of polished metal; evaporate by heat, and if no stain be left the water is pure. Distilled water is always sufficiently pure without this trial.

"After this washing the drawing is finished."

Fox Talbot does not seem to have adopted "Herschel's Hypo" as a fixing agent with the same speed as Daguerre. In Talbot's patent for the calotype process (February 8, 1841) we find:

"*The Fixing Process.*—The picture is dipped into water, partly dried, washed with a solution of bromide of potassium or some other soluble bromide, washed with water, and finally dried:"

But two years later (June 1, 1843) we actually find Talbot *patenting* the discovery of Herschel. The patent was for nine improvements in the calotype process: "1st. To give increased whiteness to calotype and other photographic pictures, and at the same time make them more permanent, they are plunged into a hot solution of hyposulphite of soda (or any other soluble hyposulphite), then removed, washed and dried." In the "ninth improvement" we are told that: "The negative copy upon 'copying paper' is fixed by being washed with warm water, placed in a solution of hyposulphite of soda, and all removed that is soluble in water by plunging it into two or three baths of warm water consecutively."

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* If hyposulphite has been used, the distilled water need not be so hot as when common salt has been employed.

Of course, such a patent could not be valid; but it has, unfortunately, been too much the practice for the English Patent Office to grant letters-patent without making any proper inquiry into the originality of the invention claimed. Talbot never attempted to enforce this claim for the use of hypo as a fixing agent.

Talbot does not seem to have been well "advised" in the procuration of his patents, for on December 12, 1849, we find him including in a patent a claim for: "A method of obtaining more complete fixation of photographic pictures upon paper. In addition to the usual fixing process, the picture is dipped into a boiling solution of caustic potash." This particular point, however, we find him "disclaiming" on May 1, 1855.

How to Fix Photographs.

The "hypo" bought should be in *clear* crystals, and should not be too cheap. In England "hypo" can be bought at from one to six cents per pound; and the better quality is worth the money. Thoroughly pound the crystals in a mortar, and make up the solution in the proportion of four ounces of solid hypo to twenty ounces of ordinary water. Add a teaspoonful or so of ammonia to every quart of the solution; for acid hypo is a thing to be avoided, and the alkali also helps to prevent blistering. A solution of this strength (1 to 5) is just right for fixing negatives. But for paper prints it should be reduced by adding half as much more water, so as to bring down the strength to 1 to 7½.

When a negative or a print is placed in an ample supply of such a solution, the result is the formation of silver sodium hyposulphite:

$AgBr$	+	$Na_2S_2O_3$	=	$AgNaS_2O_3$	+	$NaBr$
Silver bromide	*and*	Sodium hyposulphite	*produce*	Double hyposulphite of silver and sodium	*and*	Sodium bromide.

This double hyposulphite is very soluble in water, and is easily washed out of the film.

But if an insufficient amount of hypo be employed another compound (Ag_2Na_4, 3 [S_2O_3]) is formed, which is *insoluble* and cannot be got rid of. Let a sensitized collodion (wet) plate be half-immersed in a strong solution of hypo for five minutes; it will become quite clear, all the silver being dissolved out. Now immerse the other half of the plate in a very weak (say, one per cent.) solution of hypo, and it will be seen to be covered with a blackish deposit of the insoluble double salt—Ag_2Na_4, 3 (S_2O_3).

It may be reckoned that one ounce of solid hypo will fix three sheets of sensitized paper, or half a dozen quarter-plate negatives. Each negative should be left in the solution until it *looks* quite clear, for which about ten minutes is usually necessary. It should then be removed to a *second* bath of hypo, and left there for the same length of time. As soon as the first bath begins to fix slowly, it should be thrown away. The same plan should be adopted for prints. It is probable that much of the fading so commonly seen in both negatives and prints is due to *insufficient fixation.* It is easy enough to note the disappearance of the white silver salt from a negative, by looking at the *back* of the plate or film. But with paper prints the only guide is a greater clearness and transparency of the print, as seen when looking through it. In each case the best plan is the use of frequently renewed solutions; and the use of *two* baths, with an adequate time (not less than ten minutes) in each.

Vessels of tin or zinc should never be used as fixing baths; the hypo corrodes them; and the prints then stain when they touch the corroded surface. Baths made of lead, with vertical grooves are convenient.

Should the ordinary fixing bath become acid the following chemical reaction will take place.

$Na_2S_2O_3$	+	$2HCl$	=	S	+	SO_2
Sodium hyposulphite	*and*	Hydrochloric acid	*produce*	Sulphur	*and*	Sulphur dioxide
			+	$2NaCl$	+	H_2O
			and	Sodium chloride	*and*	Water.

Other acids act in a similar way to the one—hydrochloric acid—here selected as an example. The sulphur deposited will combine with the finely divided black silver which forms the picture, to produce sulphide of silver, a compound which, when in extremely thin layers, has a yellowish hue. This is the reason why the simple hypo bath should always be kept alkaline.

If hypo crystals effloresce, or become covered with a white powder when left exposed to the air, it is a sign that they contain Glauber's salt (sulphate of soda). If such be the case, a larger quantity of the hypo must be used in making up the fixing solution, as Glauber's salt has no power as a fixing agent. Hypo does not keep well in solution, and light hastens its decomposition. It is well, therefore, to paste brown paper round the store bottles, and to make up fresh solutions every two or three weeks. The hypo which has been used for fixing prints may be used afterwards, if its strength is not exhausted, for fixing negatives, but not *vice versa*.

In 1866* Mr. John Spiller recommended the addition of a little carbonate of ammonia to the hypo fixing bath, which he thought would "serve a useful end firstly, by aiding the hyposulphite in the more perfect removal of the silver; and, secondly, by rendering more permanent the double soda and silver salt so formed." About half an ounce of the ammonium carbonate should be ground to powder and added to each quart of the hypo solution. The prints, after washing, should be sponged in order to remove a very slight whitish veil, which sometimes results from this employment of the carbonate.

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* *British Journal of Photography* for June 15, 1866.

There is no doubt but that in the case of albumenized sensitized paper a small portion of the silver enters into combination with the albumen to form a complex compound called albuminate of silver; a compound which it is difficult, if not impossible, to remove, and which probably contributes to the fading of such prints.

As far back as 1862 we find that well-known chemist, Mr. John Spiller, writing*: "Proceeding in the next place to inquire into the disposition of the silver and gold upon the surface of albumenized proofs, I have been somewhat surprised to find so much silver existing in the sky and other perfectly protected portions of the print,† an observation which led me to examine a large number of photographs, and cuttings removed from the same, preliminary to mounting, also the productions of other operators besides the work executed by our own department; and in no instance have I failed to detect silver by the discoloration on moistening the albumenized surface with sulphide of ammonia, and allowing this reagent to dry upon the paper. But if prints upon plain paper be similarly tested there is no evidence of any silver remaining in the white parts of the picture, nor on the back or unprepared side of albumenized prints will any silver be found, a conclusive proof that the same treatment which effectually removes the whole of the silver from plain paper in the course of fixing and washing, is not capable of dissolving out entirely the silver from albumenized surfaces.

"As a confirmatory experiment, however, I sensitized plain salted paper and three different samples of albumenized paper in the same nitrate of silver solution, and, as soon as dry, they were, without exposure to light, all washed together in several changes of common water, then fixed in a newly-made solution of hyposulphite of soda (one ounce of the crystals to four ounces of water) and again repeatedly washed as usual, until, after a twenty-four hours' interval and a plentiful supply of water, they were judged to have been sufficiently washed. When dry, the sheets of albumenized paper contained silver in quantity sufficient to give a dark stain with sulphide of ammonium, whilst the plain paper did not contain a trace.

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* *Photographic News* for October 3, 1862, p. 471.

† See also Carey Lea in *British Journal of Photography* for July 27, 1866.

"Since making this observation I have endeavored to find some ready means of separating this last portion of metal from its combination with albumen, and have subjected the sample of paper to treatment with hot and cold salt brine, tartaric acid, the tartrates, and a variety of other salts, without any appreciable effect; a second immersion in hyposulphite of soda removes some of the silver; and iodide of potassium, and the citrates appear to dissolve out a larger proportion, but I am still in search of a solvent which is at once both cheap and efficient.

"As to the disadvantages arising from the existence of silver in the pure whites of the photograph, it must be remembered that they are always liable to discoloration by exposure to an impure atmosphere, and likewise by the effect of sulphur contained in the albumen itself as a constituent, which, if liberated by incipient decomposition or other cause, would immediately unite with the silver, and give rise to those yellow appearances so commonly observed in the early stages of fading."

In the same periodical for 1864 (page 22), Mr. H. Matheson stated that he had prevented discoloration of the whites of albumenized prints by soaking them, after toning, in a "solution of twenty grains of potassium iodide in about a pint of water for five minutes," and then fixed them in hypo as usual.

Replying to this on February 12, 1864 (page 74), Mr. Spiller states that although such treatment might be effective in removing any traces of "free nitrate," yet it could not remove "that small proportion of silver which always enters into chemical combination with the albumen, and is not afterwards soluble in the hyposulphite of soda."

GAUDIN INTRODUCES FIXING WITH CYANIDE OF POTASSIUM.

Potassium cyanide as a fixing agent was used mainly in connection with the positive wet-collodion process. The first reference I can find to it is in the French periodical, *La*

Lumière, for April 23, 1853, where M. Gaudin recommends it strongly as being "more convenient and more economical" than hypo. It was used in the proportion of eight or ten grains to the ounce of water, and was poured upon the developed wet-collodion plate while the latter was held level by one corner. The solvent power of potassium cyanide upon silver iodide is very great, and in a minute or two the picture was fixed. It gave a bright, clean, and vigorous picture, whiter and with more detail than hypo, and was a great favorite in consequence during the reign of the "ambrotype" (as the positive collodion photograph on glass was called) between 1853 and 1858. It still lingers, however, among the ferrotype workers, who find it useful because it does its work so quickly; a great advantage to this class, since being workers by the wayside, on the beach, etc., they desire to complete and deliver their pictures in a few minutes.

The chemical action is as follows:

$$\underset{\text{Silver Iodide}}{\mathrm{AgI}} \underset{\textit{and}}{+} \underset{\text{Potassium Cyanide}}{\mathrm{2KCN}} \underset{\textit{produce}}{=} \underset{\text{Potassium Silver Cyanide}}{\mathrm{AgK(CN)_2}} \underset{\textit{and}}{+} \underset{\text{Potassium Iodide.}}{\mathrm{KI}}$$

The potassio-silver cyanide is one of the so-called "double salts," and the important difference between it and the silver cyanide is that the former is very soluble in water, while the latter is not. Thus it is easy to wash the potassio-silver cyanide out of the film and off the plate.

But potassium cyanide is so powerful that it is able even to dissolve a little of the metallic silver forming the image, when this is in a very finely divided state.* In the case of the "ambrotypes" the deposit of silver was coarse-grained; but in the ordinary negative collodion process, and in the calotype process on paper, the deposit of silver is much finer, and when potassium cyanide is used as a fixing agent the half-tones suffer. In the case of silver bromide, and of silver chloride, the action of the cyanide is even greater, so that it is never used to fix pictures made with them. The potassium cyanide of commerce is, moreover, always alkaline—owing to the presence of carbonate of potassium as an impurity—and it has consequently a tendency to soften the gelatine film. For over-printed silver prints, however, potassium cyanide is sometimes useful as a reducer. The prints are immersed in an extremely weak solution (about one grain of cyanide to half a gallon of water) and in the course of an hour or two much of their superfluity of silver will be removed.

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* Carey Lea, in *British Journal of Photography* for September 7, 1866.

Snelling, in his "Dictionary of the Photographic Art" (New York, 1854), says:

"Cyanide of potassium is excellent, in solution, for removing—with the aid of a sable pencil—the black spots which so often spoil a good proof. The operator, however, should be careful to arrest its action at the proper moment, as if left too long it will remove too much. To do this you must wash the proof in clear water acidulated with prussic acid, and again wash it in several waters. * * * It is also used for removing stains of nitrate of silver from the hands in the proportion of one grain of the salt to ten grains of water."

Snelling adds that "Cyanide of potassium dissolves the iodide, chloride and bromide of silver," but he does not speak of it as a fixing agent, so that presumably it was little if at all employed at that time in the United States for such a purpose. Indeed, Snelling says elsewhere in his book: "Hyposulphite of soda is the best fixer that can be employed, as well for negative as for positive proofs."

A patent taken out in England by "Peter Armand le Comte de Fontaine Moreau," on December 13, 1854, directs the developed picture (a collodion positive) to be "washed several times in fresh water, and then plunged into a bath composed of cyanide of potassium and distilled water" in order to fix it.

The extremely poisonous nature of potassium cyanide is a great drawback to its general usefulness. It is, in itself, highly poisonous; but if any acid be added to it, fumes of hydrocyanic (prussic) acid are given off, the inhalation of which is usually followed by fainting and illness, and not unfrequently by death.

Many photographers have committed suicide by swallowing this deadly poison, three grains of which is a fatal dose; it lay ready to their hand, and they knew that it produced a rapid and comparatively painless death. It is better banished altogether from the shelves of the ordinary worker. The symptoms of poisoning by cyanide are "insensibility, slow, gasping respiration, dilated pupils, and spasmodic closure of the jaws." There is no certain remedy, although the flowing of a stream of cold water over the head and neck has been found useful. If the cyanide touches sore places or abrasions in the skin it produces a painful smart, which may be eased by the early application of sulphate of iron.

Water as a Fixing Agent.

The ideal fixing process—that in which the prints require nothing more than a good washing in plain water—at present belongs to one printing process only, that known as *cyanotype*, or the "blue" process.

The two salts with which the paper is coated are potassium ferricyanide and ammonio-citrate of iron, each of them soluble in water. By exposure to the light these two substances are caused to combine, when they form an *insoluble* blue compound closely allied to "Prussian blue."

The excess of soluble matter is then removed by simple washing in water, and the picture is then seen in white lines on a blue ground.

Hydrochloric Acid as a Fixing Agent.

In the "platinotype" printing process we coat paper with ferric oxalate (which is converted into ferrous oxalate by the action of light) and chloro-platinite of potassium. The picture is ultimately produced (by floating the exposed print upon a bath of hot oxalate of potash) in metallic platinum. The iron, etc., salts which remain are soluble in a weak solution of hydrochloric acid (1 to 60), and the prints are allowed to soak in this for a few minutes until their yellow hue (due to the iron) has completely disappeared. Finally they are well washed for half an hour in plain water to remove the acid.

THE ACID SULPHITE FIXING BATH.

In the early part of the year 1889 several articles appeared in the German photographic papers (*Photographische Correspondenzen*, *Archiv*, etc.), principally from the pen of Dr. Alexander Lainer, recommending the addition of acid sodium sulphite to the ordinary hypo bath for fixing negatives. The advantages were said to be that the plates were both fixed and *cleared*, and that the fixing bath remained clear and in good order for a longer period.

Sodium sulphite (Na_2SO_3) has long been used to keep the pyro solution clear during development; and *acid* sodium sulphite ($Na HSO_3$) can be made by adding an acid—preferably tartaric acid—to the solution of the sulphite.

Lainer recommends that the acid fixing bath be made up as follows:

1. Make up thirty-four ounces of an ordinary hypo bath, strength one ounce of hypo to four ounces of water.

2. Make solutions of tartaric acid and of sulphite of soda, each of the same strength (1 to 4).

Mix one ounce of the tartaric-acid solution with two and a half ounces of the sulphite solution; shake well and then add the mixture to the thirty-four ounces of hypo solution. Hydrochloric acid may be used instead of tartaric.

The acid sulphite is also sold commercially as a lye, in which state it is a pale yellowish liquid, smelling strongly of sulphurous oxide gas. With this it is only necessary to add two ounces of the lye to each quart of hypo solution. Besides the advantage already named, this "acid fixer" fixes very rapidly.

The use of the acid in the bath is really to liberate sulphurous acid (SO_2), a substance which has powerful decolorizing properties. This acid was recommended in 1885* for use in the clearing bath, instead of the citric or hydrochloric acid as usually employed. In December, 1887, the late Mr. H. B. Berkeley patented a combination of hypo and free sulphurous acid as a fixing agent. Sulphurous acid, unlike most other acids, does not decompose hypo, and therefore the liberation of sulphur, with its baneful effect upon the negative, is not to be feared.

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* *British Journal of Photography* for June, 1885 (editorial).

Why do Photographs Fade?

The early photographers took but little pains to get rid of the excess of hypo with which their prints were impregnated. It is true that in the case of collodion positives a good washing and rinsing will remove the hypo from the porous and inert collodion in a few minutes, but in the case of paper the hypo clings more obstinately to the fibres.

About the year 1854 the general fading of paper prints had become so evident, that the Photographic Society of London appointed a committee to "take into consideration the question of the Fading of Positive Photographic Pictures upon Paper." The report of this committee is published in the Society's journal for November 21, 1855, and the following eminent names are appended to it: Delamotte, Dr. Diamond, T. F. Hardwich, Malone, John Percy, H. Pollock, Geo. Shadbolt.

The report is so important—and withal so compact—that we reproduce it in full:

"The Committee, in this Report, propose to confine themselves to a statement of the evidence which they have collected as to the permanence of photographs up to the time of their appointment, adding some facts in connection with the causes of fading, which are of practical value, reserving for a future occasion the scientific part of the investigation.

"*Evidence of Permanence.*—The Committee have unquestionable evidence of the existence of photographs which have remained unaltered for more than ten years,[*] prepared by salting plain paper with a chloride, afterwards making it sensitive with either nitrate or ammonio-nitrate of silver, mixing with a freshly made solution of hyposulphite of soda and washing in water; also of positives[†] produced by Mr. Talbot's negative process.

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[*] That is, since 1845. W. J. H.

[†] *i.e.*, developed prints. W. J. H.

"They have not been able to obtain evidence of photographs having been prepared at all upon albumenized paper,* or colored with a salt of gold or fixed with 'old hypo,' so long ago as ten years.

"They have, however, ample evidence of the existence of unaltered photographs so prepared, five, six, or seven years ago.

"They have not found that any method of printing which has been commonly followed, will necessarily produce fading pictures, if certain precautions be adopted; nor have they evidence that any method which has been adopted, will not produce fading pictures unless such precautions are taken.

"*Causes of Fading.*—The most common cause of fading has been the presence of hyposulphite of soda, left in the paper from imperfect washing after fixing.

"The committee think it right to state, that they have been unable to find any test to be relied upon, which can be used to detect a minute portion of hyposulphite of soda, in the presence of the other substances which are obtained by boiling photographs in distilled water and evaporating to dryness; yet they have no doubt of the truth of the above statement, from the history given of the mode of washing adopted.

"The continued action of sulphuretted hydrogen and water will rapidly destroy every kind of photograph; and as there are traces of this gas at all times present in the atmosphere, and occasionally in a London atmosphere very evident traces, it appears reasonable to suppose that what is effected rapidly in the laboratory with a strong solution of the gas, will take place also slowly but surely in the presence of moisture, by the action of the very minute portion in the atmosphere.

"The committee find that there is no known method of producing pictures which will remain unaltered under the continued action of moisture and the atmosphere in London.

"They find that pictures may be exposed to dry sulphuretted hydrogen gas for some time with comparatively little alteration, and that pictures, in the coloration of which gold has been used, are acted upon by the gas, whether dry or in solution, less rapidly than any others.

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* Such paper, coated with white of egg to give it a gloss, and to prevent the silver salt from sinking too deeply into the paper, was introduced about 1852. The use of chloride of gold for toning paper prints became general about the same time. W. J. H.

"They also find that some pictures which have remained unaltered for years, kept in dry places, have rapidly faded when exposed to a moist atmosphere.

"Hence it appears that the most ordinary cause of fading may be traced to the presence of sulphur, the source of which may be intrinsic from hyposulphite left in the print, or extrinsic from the atmosphere, and in either case the action is much more rapid in the presence of moisture.

"*Mode of Mounting Photographs.*—The committee find that taking equal weights, dried at a temperature of 212 deg. of the three substances most frequently used, viz: gelatine, gum, and paste, the latter attracts nearly twice as much moisture as either of the former; and as in practice a much smaller weight of gelatine is used than of gum, gelatine appears to be the best medium of these three; and the Committee have evidence of fading having in some cases been produced by the use of paste.

"In illustration of some of the circumstances alluded to above, the Committee think it well to mention some instances of prints at present in their possession.

"Out of several prepared together in 1844, three only are unaltered, and these were varnished soon after their preparation with copal varnish.

"Half of another print of the same date was varnished, and the other half left; the unvarnished half has faded, the varnished remains unaltered.

"Three pictures were prepared in 1846, all at the same time, with the same treatment; when finished, one was kept unmounted; the other two were mounted with flour-paste at the same time, one of these latter having been first coated with Canada balsam; at present the unmounted one and the one protected with balsam are unchanged, whereas the other has faded.

"A picture prepared in 1846 was so exposed that the lower part of it became wetted with rain; at present the part so wetted has faded, while the rest of it remains unaltered. Several pictures were prepared and mounted about ten years ago, and kept in a dry room for about three years without any change, after which they were placed in a very damp situation, and then faded decidedly in a few months.

"The Committee propose very shortly to actually test the durability of the various modes of printing, by exposing pictures to different treatment, and they have been fortunate enough to obtain a grant of space for this purpose from the Crystal Palace Company.

"The Committee make the following suggestions, arising out of the above report:

"1. That the greatest care should be bestowed upon the washing of prints after the use of hyposulphite of soda, and for this purpose hot water is very much better than cold.

"2. The majority of the Committee think that gold, in some form, should be used in the preparation of pictures, although every variety of tint may be obtained without it.

"3. That photographs be kept dry.

"4. That trials be made of substances likely to protect the prints from air and moisture, such as caoutchouc, gutta percha, wax and the different varnishes."

The simple conclusions arrived at in this able report are as true to-day as they were thirty-eight years ago. Of course they apply—as the report applied—to ordinary silver prints only. Hypo left in the print; plus sulphuretted hydrogen (from burning gas-jets, etc.), and moisture in the air; these are the great enemies of silver prints; and they combine—sooner or later—to reduce the brilliant silver print to a yellow faded shadow of its former self. Sulphur is liberated from either hypo or sulphuretted hydrogen, and it combines with the black silver which forms the picture to produce the yellow or yellowish-brown compound known as sulphide of silver (Ag_2S).

We have, it is to be feared, not arrived much nearer the solution of a "permanent printed-out silver print on albumenized paper" since the report quoted above was prepared in 1855. The remedy, to the more earnest workers of the present age, seems to be to discard this printing process altogether. The meretricious gloss of the paper is as inartistic as the pictures printed upon it are fleeting.

Prints on matt-surface paper seem to be somewhat more permanent than those on albumenized paper, the reason being that albumen itself contains a little sulphur (witness the blackening of our silver egg-spoons) and is a substance very liable to decomposition; while the developed prints on bromide paper are certainly far more lasting. But the prints produced by the "platinotype" process, and by the "carbon" process, are the only ones which can be guaranteed with certainty to be as permanent as engravings.

However, much might be done to lengthen the lives of silver prints, and to "give them a fair chance." To remove the hypo thoroughly the prints ought to be frequently *pressed*, as well as washed in many changes of water. Capt. Abney uses a sponge,* and with it presses the print upon a glass plate some ten or twelve times, allowing the print to soak in fresh water for ten minutes between each squeezing. It is also an excellent plan to soak the prints alternately in *hot* and *cold* water.

Then the cardboard on which the print is mounted ought to be free from injurious chemicals (hypo itself is much used in the manufacture of paper and cardboard); the mountant should be suitable (as starch, or gelatine) and freshly made; and, lastly, the picture should be protected from the air by being well framed, or by means of a good album.

Still, "give up the ordinary printing process on (silver) sensitized paper" is our advice to all who desire their work to "live after them."

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* A soft roller squeegee acts as well as or even better than a sponge.

CHAPTER XXXIV.

THE CHEMISTRY OF HYPO ELIMINATORS.

ATTEMPTS TO REMOVE HYPO BY CHEMICAL MEANS.

The length of time—twenty-four hours, according to many writers—required to remove the last traces of hypo from prints by the action of water alone, and the physical exertion needed when such a plan as sponging or pressing the prints is adopted, have led to many attempts to find some speedy and effective means of removing this treacherous fixing agent from the paper. In effecting the removal or destroyal of hypo these plans are for the most part effective; but they are, unfortunately, apt to introduce at the same time other chemical compounds whose presence may be even more harmful.

Peroxide of Hydrogen.—At a meeting of the Photographic Society of Scotland on May 8, 1866, a paper sent by Dr. Angus Smith, of Manchester, was read,* in which he recommended a solution composed of one part of the liquid peroxide (as sold commercially) to one thousand parts of water as a means of oxidizing the hyposulphites remaining in the prints into "innoxious and harmless sulphates." Peroxide of hydrogen ($H_2 O_2$) was then sold at five shillings per pound, but it is now (1892) only two shillings per pound. It is a substance which is very unstable, and in the presence of the other chemicals it decomposes into water and oxygen as follows:

$$\underset{\text{Hydrogen Peroxide}}{H_2 O_2} \quad \underset{\textit{produces}}{=} \quad \underset{\text{Oxygen}}{O} \quad \underset{\textit{and}}{+} \quad \underset{\text{Water.}}{H_2O}$$

The oxygen then combines with the hypo:

$$\underset{\substack{\text{Sodium Hypo-}\\\text{sulphite}}}{Na_2S_2O_3} \quad \underset{\textit{and}}{+} \quad \underset{\text{Oxygen}}{2O_2} \quad \underset{\textit{and}}{+} \quad \underset{\text{Water}}{H_2O} \quad \underset{\textit{produce}}{=} \quad \underset{\substack{\text{Sodium Hydrogen}\\\text{Sulphate.}}}{2Na\,HSO_4}$$

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* See *British Journal of Photography* for 1866, pp. 226, 232, 267, 316, 327.

The sodium-hydrogen sulphate is readily removed from the paper by a short washing in water; but even if any be left in the print it would be comparatively harmless.

The objections to the use of hydrogen peroxide as a hypo eliminator are that it is liable to destroy the more delicate half-tones of the image, and that it does not keep well. Where hydrogen peroxide cannot be bought, it may be readily prepared by mixing one ounce of glacial acetic acid with four ounces of *cold* water and adding one ounce of powdered barium dioxide. The prints should be immersed in this solution for five minutes.

Sodium and Other Hypochlorites as Eliminating Agents.—In 1864 Mr. F. W. Hart told the members of the South London Photographic Society (see *British Journal of Photography* for March 1, 1864) that "with the desire, if possible, to secure the permanency of silver prints, he had experimented as follows: Two prints were taken (for which the paper had been prepared in the usual way) and treated throughout in an exactly similar manner up to the point of toning, when one, after being toned, was immersed in hyposulphite of soda, rinsed, and then immersed in an aqueous solution of chlorine and chloride of barium. The effect of this treatment he (Mr. Hart) had found to be the conversion of any remaining traces of hyposulphite of soda into sulphate of barium and chloride of sodium, thereby insuring the non-existence of sulphur in the prints."

We cannot hear of this plan having been adopted by any one. The free chlorine would probably affect the half-tones of the prints considerably.

But in 1866 the same worker (Mr. F. W. Hart) proposed a method which has been more generally tried, though it cannot be said to have been adopted to any extent. Mr. Hart's second proposal, read as a paper before the South London Photographic Society (see *British Journal of Photography* for June 22, 1866; see also editorial article in number for June 29, 1866), was on the subject of "The Elimination of the Double Hyposulphites of Soda and Silver from Photographic Prints." The substance now proposed to be used for this purpose was hypochlorite of soda. When this is brought into contact with hypo the following reaction occurs:

$$\underset{\text{Sodium Hypochlorite}}{4NaClO} \underset{\textit{and}}{+} \underset{\text{Sodium Hyposulphite}}{Na_2S_2O_3} \underset{\textit{and}}{+} \underset{\text{Water}}{H_2O} \underset{\textit{produce}}{=} \underset{\text{Sodium Chloride}}{4NaCl} \underset{\textit{and}}{+} \underset{\text{Sodium Hydrogen Sulphate.}}{2NaHSO_4}$$

Sodium hypochlorite is sold commercially as "Labarraques' solution." It can readily be prepared by dissolving a quarter-pound of carbonate of soda in ten ounces of water, and two ounces of chloride of lime in thirty ounces of water. Mix, boil, and filter.

Other hypochlorites have since been introduced; and in America, zinc hypochlorite, sold as "Flandreau's eliminator," has been rather a favorite. Its chemical action is as follows:

$$\underset{\text{Zinc Hypochlorite}}{2ZnCl_2O_2} \underset{\textit{and}}{+} \underset{\text{Sodium Hyposulphite}}{Na_2S_2O_3} \underset{\textit{and}}{+} \underset{\text{Water}}{H_2O} \underset{\textit{produce}}{=} \underset{\text{Zinc Chloride}}{2ZnCl_2} \underset{\textit{and}}{+} \underset{\text{Sodium Hydrogen Sulphate.}}{2NaHSO_4}$$

If this were all that could happen, then zinc hypochlorite and the other hypochlorites would be good hypo eliminators; but they do not keep well, and they are very liable to liberate free chlorine, the following *secondary* reaction then occurring:

$$\underset{\text{Sodium Hyposulphite}}{Na_2S_2O_3} \underset{\textit{and}}{+} \underset{\text{Chlorine}}{8Cl} \underset{\textit{and}}{+} \underset{\text{Water}}{5H_2O} \underset{\textit{produce}}{=} \underset{\text{Hydrochloric Acid}}{8HCl} \underset{\textit{and}}{+} \underset{\text{Sodium Hydrogen Sulphate.}}{2NaHSO_4}$$

The hydrochloric acid so formed would immediately react upon more hypo in the following way:

$$\underset{\text{Sodium Hyposulphite}}{Na_2S_2O_3} \underset{\textit{and}}{+} \underset{\text{Hydrochloric Acid}}{2HCl} \underset{\textit{produce}}{=} \underset{\text{Sulphur}}{S} \underset{\textit{and}}{+} \underset{\text{Sulphur Dioxide}}{SO_2} \underset{\textit{and}}{+} \underset{\text{Sodium Chloride}}{2NaCl} \underset{\textit{and}}{+} \underset{\text{Water.}}{H_2O}$$

Now sulphur is perhaps the most injurious substance we can possibly have in the print.*

---

* *British Journal of Photography* for October 26, 1886.

Potash hypochlorite (commercially known as eau de javelle) has also been much used as a hypo eliminator. It is easily made by dissolving a quarter of a pound of carbonate of potash in thirty ounces of water; then mix two ounces of chloride (properly hypochlorite) of lime in ten ounces of water. Mix the two liquids, boil, and filter. The chemical action is:

$$Na_2S_2O_3 + 4KClO + H_2O =$$

Sodium Hyposulphite *and* Potassium Hypochlorite *and* Water *produce*

$$4KCl + 2NaHSO_4$$

Potassium Chloride *and* Sodium Hydrogen Sulphate.

It will be seen that all these hypochlorites are of an unstable nature, readily parting with their oxygen and becoming reduced to chlorides. The liberated oxygen combines with the hypo to form a sulphate, which is a stable and comparatively harmless compound.

Iodine as a Hypo Eliminator.—Dr. H. W. Vogel was, we believe, the first to suggest the use of the elementary body, iodine, as an aid to the removal of hypo from prints. Iodine is dissolved in a strong solution of potassium iodide until a very dark-colored liquid is obtained. After careful washing the prints are placed in water to which enough of the iodine solution has been added to give it a sherry color. Here the prints take a faint blue color. They are then rinsed in a very weak solution of mixed sulphite and carbonate of soda (by which the blue color is taken out) and are finally well washed in water.

The chemical action of the iodine is as follows:

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6$$

Sodium Hyposulphite *and* Iodine *produce* Sodium Iodide *and* Sodium tetrathionate.

The two sodium salts formed (the iodide and tetrathionate) are very soluble and are easily washed out of the paper. Mr. C. B. Lloyd has strongly objected to this method* on the ground that sodium tetrathionate is a salt containing much sulphur, and that it is readily decomposed. He also thinks that the whites of the picture are degraded by the temporary dyeing with iodine.

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* *British Journal of Photography* for 1887, p. 724.

Alum as a Hypo Remover.—The first reference I can find to the use of alum as a hypo eliminator is in the *Journal of the Photographic Society* for the 21st of June, 1855, where Sir W. J. Newton recommends prints to be treated as follows: "Immerse in hyposulphite for about two or three minutes, then in alum-water for half an hour, and change the water *entirely* two or three times." Referring to this note, Mr. T. Sutton remarks in the same *Journal* for August 21: "The alum bath recommended by Sir William Newton is also a useful suggestion. The alum forms with the hypo a double salt (soda-alum), which is highly soluble in water, and I imagine comparatively innocent."

If this advice was largely acted upon it is not surprising that very few photographs printed in 1855 are in existence in 1890.

But an antidote to this "alum" method was soon supplied by T. F. Hardwich, the leading photographic chemist of that day; in the *Journal* for September 21, of the same year, he writes: "With reference to the use of *alum* in washing paper positives, may I be allowed, on chemical grounds, to raise an objection. It is *an acid salt*, the sulphuric acid being only imperfectly neutralized by alumina, which is a feeble base; hence on mixing it with hyposulphite of soda, sulphate of soda, sulphurous acid, and sulphur are formed, the reaction being the same to all appearance as that of the acids generally, upon hyposulphite of soda."

Hardwich wrote further upon the subject in the *Journal* for March 21, 1856, with the result of convincing Newton that alum did more harm than good.

Holmes' Ozone Bleach. This is a commercial preparation, the chemical composition of which has not been published. But as its name tells us that it is a product of ozone we may say that that substance is a condensed form of oxygen, each molecule containing *three* atoms of oxygen (O_3), while in ordinary oxygen the molecules consist of *two* atoms only (O_2).

Ozone is an active oxidizing agent, and it would convert hyposulphite of soda into sulphate, thus:

$Na_2S_2O_3$	$+$	$2O_3$	$+$	H_2O	$=$	$2NaHSO_4$	$+$	O_2
Sodium Hyposulphite	*and*	Ozone	*and*	Water	*produce*	Sodium Hydrogen Sulphate	*and*	Oxygen.

But the ozone is very likely to attack the delicate half-tones of the prints.

Water the best Hypo Eliminator. Having described the various means which have been suggested for getting rid of hypo, chemically, in a short time, we must own to having little belief in any of them. The so-called eliminators—while doubtless removing the dreaded hypo, *as* hypo—frequently form new compounds which may be no less dangerous. They generally damage the print in some way or other, perhaps destroying the more delicate half-tones, or injuring the purity of the whites.

Supposing the print to have been properly fixed in two baths of fresh hypo; then nothing can excel the repeated washings in changes of warm and cold water—combined with pressure—which we have recommended.

We can best conclude this part of our subject by using the words of the writer of an editorial article in a recent number of the *British Journal of Photography*.* "And what we desire to impress upon all is, that the same amount of care applied in simple washing will effect the purpose in view, the removal of the hyposulphites at least, as efficiently as any eliminator, and without any danger."

How to Detect the Presence of "Hypo" in Plates or Prints.—It is useful to have some means of determining whether we have been successful in our endeavors to wash our negatives and prints thoroughly. The following tests will indicate whether any hypo still remains in them:

The Permanganate Test.—Dissolve two grains of potassium permanganate and twenty grains of potassium carbonate in one quart of distilled water. This solution is of a fine pink color. Take the water in which the negatives or prints have last been soaking for ten minutes or more, and pour it into a clean glass bottle, which will hold, say, one pint. To this clear water add five or ten drops of the pink (permanganate) solution. If the water be pure it will assume a pale pink tinge; but if any hypo be present the color will change to a light shade of green. The bottle should be shaken well, and allowed to stand for ten minutes.

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* For 18th October, 1890.

The Starch Iodide Test.—Powder and boil a piece of starch the size of a pea in quarter of an ounce of water until a clear solution is attained. Add to this one drop of tincture of iodine (iodine dissolved in alcohol) which will produce a dark-blue color. Fill one test-tube with distilled water, and another with the water to be tested for the presence of hypo. Add to each test-tube one drop of the blue solution. If any hypo be present the blue color will disappear. The tubes should be shaken well, gently warmed, and examined side by side in front of a piece of white paper.

Hypo in Prints.—The paper used for printing photographs upon is all but invariably sized with starch. Make an extremely weak solution* of potassium iodide, and apply it with a brush to the back of the print to be tested. A blue color will indicate the *absence* of hypo.

An Electrical Test for Hypo.—In 1866 Dr. Reissig, of Darmstadt, used † a test which showed that "the amount of sulphur was very large," in several faded prints examined by means of it. The prints were soaked in water, and two strips of polished silver, connected by wires with a single galvanic cell, were then dipped into the solution. The presence of sulphur was indicated by a black stain upon one of the silver plates. Reissig patented this process in England (March 10, 1865).

Rough Test for Hypo.—If the amount of hypo remaining in a print or in a negative be at all large it may be detected by allowing the last few drops which will fall from either when drained, to drop into the mouth. Mention has already been made of the intense *sweetness* of the double salt of soda and silver which the hypo forms, and which it is our object to remove from our negatives and prints. The absence of any sweet taste would, however, only indicate that the *greater part* of the dangerous salt had certainly been removed.

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* Two grains of the salt in a pint of water.

† *British Journal of Photography*, p. 232.

Nitrate of Silver Test.—Dr. Bannon * finds that silver nitrate is a delicate test for discovering traces of hypo in prints or films. The water from the prints, etc., should be allowed to drain into a test-tube and heated, and then a few drops of silver nitrate solution added to it. A black precipitate will be formed if the one ten-thousandth part of hypo be present; while a still smaller amount will give a yellow precipitate.

LITERATURE OF FIXING PROCESSES, ETC.

In addition to the references given in the course of these articles on "The Chemistry of Fixing," we append a list of a few papers, etc., written during the last few years, which have been consulted upon the subject.

FROM THE PHOTOGRAPHIC TIMES.

The Acid Fixing Bath, Etc. (Editorial), p. 171, for 1890.

Lainer, A.—An Acid Fixing Bath without Turbidness, p. 238, for 1889.

Fading of Silver Prints, p. 540, for 1889.

Brockway, C. M.—Faded Prints, p. 533, for 1888.

Alum as a Hypo Eliminator (Editorial), p. 79, for 1887.

Hypo Eliminators; Do they Eliminate? (Editorial), p. 232, for 1887.

Sherman, W. H.—Hypo Eliminator, pp. 292, 359, 579, 660, for 1887.

FROM THE BRITISH JOURNAL OF PHOTOGRAPHY.

The Fading of Prints (Editorial), p. 177, for 1890.

Starnes, H. S.—The Probable Permanence of Plain Paper Prints, p. 85, for 1890.

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* *Photographic Times*, p. 38, for 1889.

Acid Solutions of Hypo (Editorial), p. 50, for 1890.

The Acid Fixing Bath, p. 33, for 1890.

A Substitute (Magnesium Chloride) for Hypo as a Fixing Agent (Editorial), p. 210, for 1890.

Ultimate Effects of Hypo Eliminators (Editorial), p. 225, for 1890.

Permanency of Bromide Paper Pictures (Editorial), p. 289, for 1890.

Dunmore, E.—About Hypo, p. 327, for 1890.

Burton, W. K.—A Method of Rapidly Eliminating Hypo from Silver Prints, and other Notes on Silver Printing, p. 233, for 1889.

Hypo and Hypo Solutions, pp. 360 and 389, for 1889.

Sulphurous Acid in the Fixing Bath, p. 806, for 1889.

Dangerous Hypo Eliminators, p. 678, for 1889.

Hart, F. W.—The Early History of Hypo Eliminators, p. 151, for 1888.

The Restoration of Faded Photographs, p. 337, for 1888.

Fixing Bromide Prints—A Caution, p. 709, for 1888.

Davies, W. H.—Aids to the Preservation of Photographic Prints, p. 759, for 1888.

Starnes, H. S.—Permanence of Photographic Prints, pp. 24, 70, 101, for 1888.

Elliott, Dr. A. H.—A Search for a Substitute for Hypo, pp. 539, 554, for 1887. (Read before American Convention.)

Dawson, Geo.—On the Fading of Silver Photographs, pp. 552, 600, 616, for 1887.

Harrison, W. H.—The Fading of Silver Prints, p. 824, for 1887.

An Unsuspected Cause of Fading, p. 577, for September 16, 1887.

Fixing and Washing Gelatine-Bromide Enlargements, p. 1, for January 7, 1887.

Pringle, A.—Sulphuration of Bromide and Platinum Prints, p. 2, January 7, 1887.

Berkeley, Mansfield, Etc.—Permanence of Prints, pp. 30, 45, 59, 87, 101, 110, 159.

Lloyd, C. B.—Sulphuration of Platinum and Silver Prints, p. 36, for January 21, 1887.

Starnes, H. S.—Sulphuration of Prints, p. 217, for April 8, 1887, and p. 360, for June 10, 1887.

Lloyd, C. B.—Iodine and Hypo, p. 724, for November 18, 1887.

Bridge, F. A.—Spots, Stains, and Fading, p. 775, for December 9, 1887.

Bow, R. H.—Fixing Silver Chloride Prints by Means of Solution of Ammonia, p. 231, for April 15, 1887.

Dawson, G.—Fading of Silver Prints, pp. 321, 336, 748, for 1886.

Pringle, A.—Permanence of Prints, pp. 601, 794, 813, for 1886.

Irvine, R.—How to Prevent Silver Prints from Fading, p. 732, for November 19, 1886.

Burton, W. K.—Fixing Prints, Etc., p. 616, for October 1, 1886.

On Hypo Eliminators Generally (Editorial), p. 645, for October 15, 1886.

The Hypochlorites in Photography, p. 661, for October 22, 1886.

Permanence of Gelatino-Bromide Pictures, p. 301, for May 14, 1886.

From The Photographic News.

Higgins, J. J.—The Fixing Bath, p. 732, for 1891.

Lainer, A.—A Mixed Alum and Fixing Bath, p. 538, for August 16, 1889.

Barnes, C. B.—The Fading of Silver Prints, and its Cause, p. 715, for November 1, 1889.

Debenham, W. E.—Fading of Silver Prints, p. 777, for November 22, 1889.

Gunther, H. E.—Eliminating Hypo from Prints by Means of Common Salt, p. 355, for May 31, 1889.

Jones, Chapman.—Iodine as a Hypo Eliminator, p. 795, for December 16, 1887.

Maxims for Fixing.

1. Use freshly-made "hypo"; strength 1 to 5 for negatives; 1 to 7½ for prints.

2. Keep the hypo alkaline by the addition of enough ammonia to cause it to smell faintly, say a teaspoonful to each quart.

3. Use *two* fixing baths; allow each negative (or print) to remain at least ten minutes in each of the two baths.

4. As soon as the first bath begins to fix slowly and become dark-colored, throw it away and let the second bath take its place. Make up a fresh bath to take the place of bath No. 2.

5. Do not expose negatives (or prints) to white light while fixing, or until the hypo has been rinsed off. This is especially necessary with plates that have not had an alum bath before fixing.

6. After fixing rinse the prints or negatives in several changes of water to remove the surface hypo, and then wash for six hours in running water.

7. Fresh hypo solution should be made up for each batch of prints. For negatives the same hypo bath may be used over and over again, until it begins to work slowly. The bath used for fixing prints may afterwards be used for fixing negatives; but not *vice-versa.* After all, hypo is so cheap that it is poor economy to attempt to save in it, at the possible risk of the permanency of your results.

8. Wash the prints in three or four waters *before* you put them in the fixing bath.

9. *Move the Prints* frequently while in the fixing baths. If this is not done, yellow spots and stains may be expected.

10. Don't expect that other people—a "handy boy," for example—will fix your prints, etc., as carefully as you would do it yourself. The old proverb specially holds good in photography: "If you want a thing done well, *do it yourself!*"

INDEX.

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This School instructs in the Theory and Practice of the Art-Science of Photography, at the CHAUTAUQUA ASSEMBLY GROUNDS, in Summer; the local classes at the School's Headquarters, 423 Broome Street, New York City, during the Autumn, Winter and Spring, and by the corresponding classes through Printed Lessons and the Organ of the School.

I.—The Corresponding Class, Headquarters 423 Broome Street, New York, open for admission at any time, receives instructions by twenty-four printed lessons, prescribed home practice, required reading and by correspondence with the instructor.

Course of Instruction one year, tuition fee, inclusive of books,	$7 00

II.—The Practising Class opens on July 1st, every year, and remains in session until about September 15th. Practice in studio and field. Theoretical instruction and lectures on photographic subjects.

Course of ten lessons,	$5 00
Special lessons, each,	1 00

Independent of photographic materials and the text book.

III.—The New York Classes begin November 15th and end about May 15th. The skylight room and laboratory used by these classes are on the seventh floor of No. 423 Broome Street, New York. (Take elevator.) Separate classes for ladies.

Cost of course of ten lessons, including entrance fee, text-book and materials used in demonstration,	$7 50
Special single lessons, per hour, each,	1 00
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IV.—The Post-Graduate Class course of instruction two years. Subjects: Chemistry, Photo-Chemical Processes, Optics, and Esthetics by required reading and correspondence with the Instructor.

Tuition fee, including one year's subscription to *The Photographic Times* but independent of text-books,	$10 00

After completing a regular course the student is admitted to examination and, if passed, is awarded a Chautauqua Diploma.

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